

Author Response to Comments by Anonymous Referees

We thank the referees for their suggestions and recommendations. Below are our responses to all comments.

(RC): Referee comment

(AR): Author response

Anonymous Referee #1

This paper reports results of a laboratory study of secondary organic aerosol (SOA) formation from the oxidation of a series of n-alkanes with Cl atoms in the presence of NO_x in a smog chamber. The gas-phase composition of products and SOA was analyzed using a FIGAERO-CIMS to obtain information on product molecular formulas and thermal desorption profiles, and an ACMS and SEMS were used as well. The results were then interpreted in terms of the reasonably well-established mechanism for alkane oxidation by OH radicals, with the addition of possible oligomer-forming reactions. Interesting observations are reported on chlorine-containing products, organic nitrates, other multi-generation oxygenated products, and a new 2-D format is used to present composition and thermal data. The results provide a nice comparison to OH oxidation and the molecular and thermal characterization of products may be useful for future development and testing of models for these reactions. The experiments are very well done, and the introduction, data analysis, and interpretation are thorough and clearly written. Cl oxidation of VOCs has not been well studied, and as shown here its products can differ in significant ways from OH oxidation. There is thus plenty more to be done, but this paper is a good starting point for detailed SOA chemistry studies. I think the paper can be published in ACP after the following comments are addressed.

We thank the reviewer for the detailed assessment of the manuscript. As suggested and detailed below, we have expanded the discussions on both the gas-phase oxidation chemistry and particle-phase composition.

(1, RC) In a study of the aging of pentadecane by OH/NO_x that was not cited here (Aimanant and Ziemann, AS&T, 2013), evidence was presented based on thermal desorption profiles for the presence of acetal dimers formed from cyclic hemiacetals. These would likely be very stable and so probably desorb intact. Do the authors see any evidence for such oligomers?

(1, AR): Ions consistent with acetal and hemiacetal dimers as proposed by Aimanant and Ziemann (2013) were identified in the SOA using the FIGAERO-CIMS. In addition, ions consistent with hemiacetal dimers formed via reaction between hydroxycarbonyl nitrate and hydroxy dihydrofuran as proposed by Schilling Fahnstock et al. (2015) were identified. A diagram depicting the potential formation mechanisms, Fig. S11, is added to the S.I. A discussion on oligomerization pathways and identification of oligomeric compounds is added to the main text. Bimodal thermal desorption behaviors observed for numerous ions indicate that some oligomers underwent thermal decomposition. It is difficult to estimate the fraction of oligomer that desorbed intact, given how the decomposition mode (second desorption signal peak in a thermogram) for many ions share the same T_{\max} , as illustrated in Figs. 5 and S8.

Addition of S.I. figure:

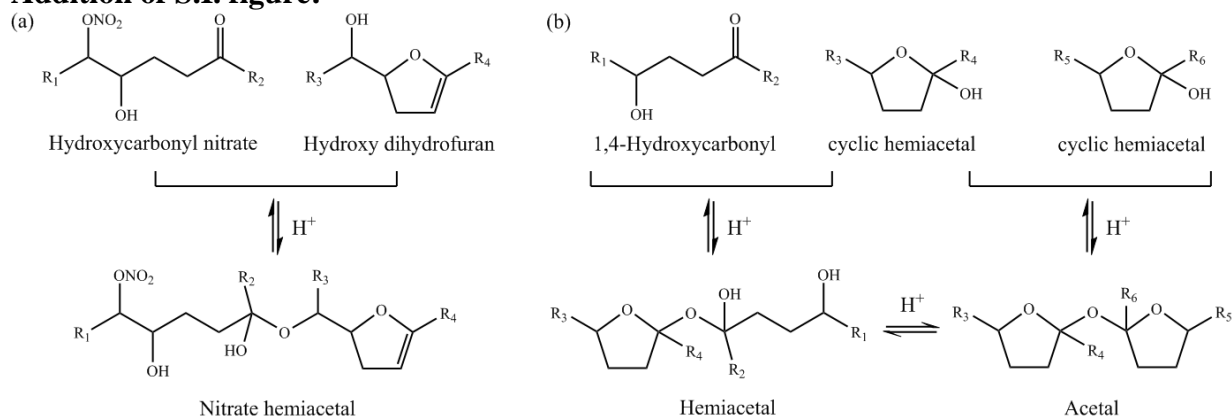


Figure S11: Oligomerization via the reaction between (a) carbonyl hydroxyl nitrate and hydroxy dihydrofuran proposed by Schilling Fahnestock et al. (2015) and (b) cyclic hemiacetal with either a 1,4-hydroxycarbonyl or another cyclic hemiacetal proposed by Aimanant and Ziemann (2013). Condensed-phase isomerization between acetal and hemiacetal dimers is also possible, as shown in (b).

Addition to Results and Discussion:

P.13, L.2 – P.14, L.7: “Oligomerization may proceed via condensed-phase reactions between cyclic hemiacetal compounds, forming acetal dimers, or reactions between cyclic hemiacetal and 1,4-hydroxycarbonyl compounds, forming hemiacetal dimers (Aimanant and Ziemann, 2013). Condensed-phase, acid-catalyzed isomerization of hemiacetal and acetal dimers is also possible (Aimanant and Ziemann, 2013). For OH-initiated oxidation of dodecane under high NO_x conditions, hemiacetals and nitrate hemiacetals are reported to dominate the oligomer composition (Schilling Fahnestock et al., 2015), where nitrate hemiacetals could form via the reactive uptake of hydroxy dihydrofuran and hydroxycarbonyl nitrate compounds (Schilling Fahnestock et al., 2015). The three oligomerization pathways are illustrated in Fig. S11. Ions consistent with acetal, hemiacetal, and nitrate hemiacetal compounds were observed in the particle phase using the FIGAERO-CIMS in regions 2 and 3. Oligomer formation via aldol condensation by highly oxidized compounds is also possible (Schilling Fahnestock et al., 2015). Oligomerization may also proceed through a NO₃-elimination, reverse esterification process involving two alkyl nitrate compounds to form a singly nitrate oligomer, which was recently proposed for α -pinene SOA, though the exact mechanism remains elusive (Faxon et al., 2018).”

(2, RC): *Can the composition data be used to estimate average molecular weights for the SOA analyzed by the FIGAERO-CIMS? It would be useful to use these values to convert the mass yields of SOA to molar yields of SOA, since this gives a better indication of the efficiency of SOA formation. Otherwise the large mass yields (due in large part to the extensive oxidation) give the impression that a large fraction of the alkane is converted to SOA, which is not really true.*

(2, AR): Based on FIGAERO-CIMS data, assuming equal sensitivity for all ions, the average molecular weight, mw_{avg} is estimated based on the desorption intensity I_i and the molecular weight, mw_i of all ions identified,

$$mw_{avg}(T_d) = \frac{\sum_i mw_i \times I_i(T_d)}{\sum_i I_i(T_d)}$$

where mw_{avg} and I_i vary with desorption temperature, T_d during a single FIGAERO desorption. A single average molecular weight for the entire FIGAERO desorption run can be calculated based on the integrated values over the T_d range,

$$mw_{SOA} = \frac{\int (\sum_i mw_i \times I_i(T_d)) \Delta T_d}{\int (\sum_i I_i(T_d)) \Delta T_d}$$

where ΔT_d is the step change in desorption temperature. It should be noted that because of thermal decomposition, which has been observed for monomers as well (Stark et al., 2017), the mw_{avg} and mw_{SOA} calculated using the FIGAERO-CIMS data likely underestimate the actual average SOA molecular weight. For octane SOA, mw_{SOA} calculated in this way ranges from 206 to 226 g mol^{-1} ; for decane SOA, mw_{SOA} ranges from 241 to 265 g mol^{-1} ; for dodecane SOA, mw_{SOA} ranges from 260 to 270 g mol^{-1} . The molar SOA yield can then be calculated as,

$$Y_{molar} = \frac{n_{SOA}}{\Delta n_{VOC}} = \frac{m_{SOA}/mw_{SOA}}{\Delta m_{VOC}/mw_{VOC}} = Y \frac{mw_{VOC}}{mw_{SOA}}$$

where n_{SOA} and n_{VOC} are the molar concentrations of SOA and VOC. The molecular weight of VOC, mw_{VOC} is known for the alkane precursors. The corresponding molar yield ranges from 0.08 to 0.14 for octane SOA, 0.26 to 0.47 for decane SOA, and 0.72 to 1.04 for dodecane SOA. The above-unity molar SOA yield observed for dodecane (Exp. 9) indicates that SOA mass may be overestimated, which may be the result of uncertainties with the collection efficiency (CE) and relative ionization efficiency (RIE) assumed for the SOA, which are addressed by (7. AR) below in response to (7. RC). The method described above is added to the section S3 in the S.I. Results are tabulated in Table S1.

(3, RC): Is there any indication for chemistry occurring between Cl, O2, and NOx? Would this be expected?

(3, AR): Ions consistent with Cl and/or NO_x oxidation products, including HNO_3 , ClONO (or ClONO₂), ClO, HONO, HO₂NO₂, and N₂O₅ were observed with the I⁻ CIMS, which are consistent with literature findings. Selected time-series are added to Fig. 1 in the main text and to Fig. S12 in the S.I.. The results suggest that secondary HO_x chemistry and perhaps NO₃⁻ chemistry (in the dark) may be important, which warrant future investigations. Discussion of the interactions between Cl, O₃, and NO_x are added to the main text.

Updates to Fig. 1:

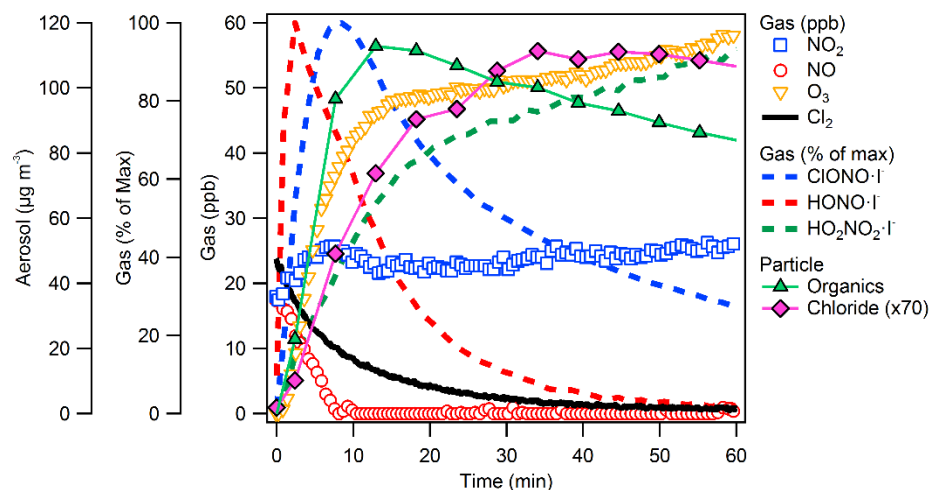


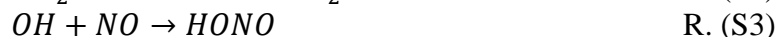
Fig 1. Representative trends of SOA and trace gas species during the photooxidation period. Data from dodecane oxidation (Exp. 11) are shown. Particulate chlorine concentrations were multiplied by 70 for ease of comparison. Observation of select ions such as HONO and HO₂NO₂ are indicative of secondary HO_x chemistry. Formation of ClONO from the interaction between Cl^{*} and NO₂ was also observed.

Addition to the S.I.:

Formation of HO₂NO₂ likely proceeds via



Formation of HONO under UV can proceed via



The trends for HO₂NO₂, HONO, and select gas-phase species observed by the I⁻ CIMS are shown in Fig. S12.

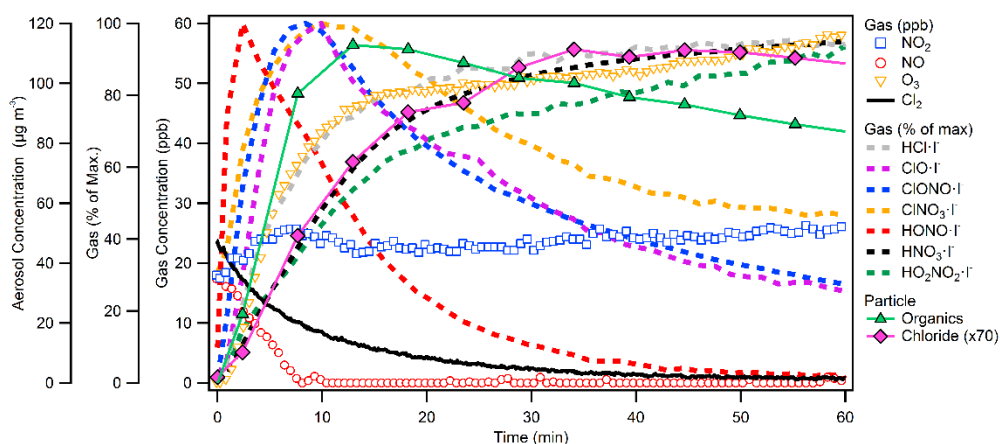


Fig. S12: Representative trends of SOA and trace gas species during the photooxidation period. Data from dodecane oxidation (Exp. 11) are shown, similar to Fig. 1 in the main text. Additional species shown include ClONO₂ (from reaction between ClONO with NO₂, Lesar et al., 2006), ClO (possibly a ion fragment of ClONO), HCl (from H-abstraction by Cl^{*} or perhaps Cl-elimination reactions), and HNO₃ (due to the oxidation of NO₂ by OH).

Addition to Results and Discussion:

P.8, L.12 – 19: “In addition, ions consistent with HO₂NO₂, HONO, and ClNO₂ were observed in the gas phase, as shown in Fig. 1. The ClNO₂I⁻ ions are expected to correspond to both ClNO₂ (< 20 %) and chlorine nitrite (ClONO, > 80 %) from the reaction between Cl[•] and NO₂ (Golden, 2007; Niki et al., 1978). Formation of HO₂NO₂ from the reaction of HO₂ and NO₂ has been observed using I⁻ CIMS previously (Veres et al., 2015). Formation of HONO was likely due to the interactions between HO_x and NO (see R. S2 and R. S3 in the SI). Under UV, HONO decays to background level. Production of HO₂NO₂ and HONO is indicative of secondary HO_x chemistry enabled by primary Cl-alkane oxidation chemistry, consistent with previous studies (Wang and Hildebrandt Ruiz, 2017; Young et al., 2014).”

(4, RC): Structure-activity relationships for the reactions of alkanes with Cl atoms indicate that the ratio of rate constants for abstraction of primary/secondary H-atoms is significantly smaller than for OH reactions, indicating that more reaction occurs at the ends of the alkanes with Cl than with OH. Have the authors considered what the consequences of this might be with regards to the products being formed?

(4, AR): With increased terminal H-abstraction by Cl radicals as compared to OH-radicals, we would expect increased primary alkyl nitrate formation. This should result in lowered saturation vapor pressure of the oxidation products (Lim and Ziemann, 2009b; Yeh and Ziemann, 2014, 2015), consistent with the higher SOA yield observed here. We have added a discussion of this factor to the main text.

Addition to Introduction:

P.3, L.9 -12: “According to structure-activity relationships, terminal hydrogen abstraction occurs more frequently with alkane-Cl than with alkane-OH reactions (Kwok and Atkinson, 1995), resulting in different product distributions; for example, increased formation of primary alkyl nitrates.”

Addition to Results and Discussion:

P.9, L.14 – 17: “Formation of primary alkyl nitrates due to terminal H-abstraction by Cl could contribute to the higher SOA yields observed for alkane-Cl than for alkane-OH oxidation, as primary alkyl nitrates have lower saturation vapor pressures than secondary alkyl nitrates (Lim and Ziemann, 2009b; Yeh and Ziemann, 2014, 2015).”

(5, RC): Have the authors considered comparing vapor pressures estimated from the measured desorption temperatures with those predicted from proposed molecular structures and the SIMPOL group contribution method?

(5, AR): Previous FIGAERO-CIMS studies show that vapor pressures calculated using either the C^{*}-T_{max} correlation or the direct partitioning method (Lopez-Hilfiker et al., 2015) can have significant disagreements with SIMPOL results (D’Ambro et al., 2017; Stark et al., 2017), which have been mostly attributed to the effects of thermal decomposition. Another complication with C^{*} estimation can also arise from potential filter loading dependence for T_{max} (Huang et al., 2018

and this work). In our opinion, this requires further investigation before vapor pressure measurements by FIGAERO and SIMPOL may be reconciled.

(6, RC): It would be useful to provide a little more detailed speculation on the proposed nature of the thermal decomposition products. Are these thought to be formed by simple reversible dissociation of hemiacetals, for instance, or by cleavage of strong C-C or C-O bonds? Or might they just be compounds that are “trapped” in a solid SOA matrix that cannot escape until the SOA melts?

(6, AR): Given that numerous organic ions exhibit bimodal thermal desorption behavior, it is reasonable to attribute it to the reversible dissociation of oligomers, a phenomenon that has been observed in the FIGAERO at room temperatures (Schobesberger et al., 2018) and at high desorption temperatures (Faxon et al., 2018). Decomposition of pure monomeric organic acids has also been reported previously, indicating that cleavage of C-C and C-O bonds (C-OH or C-OOH) does occur in the FIGAERO (Stark et al., 2017). Trapping of molecular compounds inside the SOA matrix may be possible if the aerosol existed in a “glassy state”, and could result in a sudden release of volatilized vapors (all having similar T_{\max} , as seen in region 1 and 3) though the aerosol phase state cannot be evaluated based on data available. It is worth noting that ions associated with ammonium sulfate decomposition all share the same T_{\max} with or without SOA present (that is, uniform T_{\max} can be the result of thermal decomposition as well).

Addition to Results and Discussion:

P.13, L.28 – P.14, L.4: “The thermal decomposition products may be the result of reversible dissociation of oligomers (Faxon et al., 2018; Schobesberger et al., 2018) or the cleavage of C-O or C-C bonds, which has been observed in the thermal decomposition of monomeric organic acids (Stark et al., 2017). Additionally, SOA may exist in a “glassy” state (Koop et al., 2011), trapping volatile components (Perraud et al., 2012) that are released as the SOA mass is depleted.”

(7, RC): I did not see a quoted density for calculating SOA yields from SEMS data. This value and its source should be noted.

(7, AR): The SOA yield was calculated from the ACSM measurement of organic aerosol concentration, assuming a collection efficiency, CE of 0.5 and a relative ionization efficiency, RIE of 1.4. The average, apparent SOA density calculated using ACSM and SEMS data is around $2.1 \pm 0.3 \text{ g cm}^{-3}$, which is higher than the densities previously reported for OH-alkane SOA formed under high NO_x conditions, 1.06 to 1.28 g cm^{-3} (Lim and Ziemann, 2009a; Loza et al., 2014). The discrepancy can result from the differences in SOA composition, aerosol oxidation state (Kuwata et al., 2012), or from instrument uncertainties. For instance, studies report that RIE of organics may depend on the aerosol oxidation state of carbon (Li et al., 2018; Xu et al., 2018). For $-1 < \text{OS}_C < 0.5$, which overlaps with the average OS_C as indicated by the FIGAERO-CISM measurement as shown in in Fig. 4d, the average RIE is reportedly 1.6 ± 0.5 instead of 1.4 (Xu et al., 2018), which is higher than the RIE value of 1.4 assumed here. Recalculation using the updated RIE value would lower the apparent SOA density closer to agreement with previous studies. Without an independent measurement for particle mass (e.g.

using a particle mass analyzer), it is not possible to ascertain the exact SOA density. Additional discussion associated with SOA quantification are added to the main text.

Additions to Methods:

P.5, L.23 – 25: “Organic aerosol concentrations were calculated using ACSM measurements assuming a collection efficiency of 0.5 and RIE of 1.4, corrected for depositional particle wall loss...[]”

Additional to Results of Discussion:

P.9, L.17 – 26: “The apparent SOA density, calculated using the ACSM SOA mass measurement and the SEMS SOA volume measurement, was $2.1 \pm 0.3 \text{ g cm}^{-3}$, which is substantially higher than that reported for OH-alkane SOA formed under high NO_x conditions, 1.06 to 1.28 g cm^{-3} (Lim and Ziemann, 2009a; Loza et al., 2014). These differences could be due to uncertainties associated with the ACSM and similar instruments, specifically the RIE (Li et al., 2018; Xu et al., 2018) and CE (Docherty et al., 2013; Middlebrook et al., 2012; Robinson et al., 2017), which may vary with SOA composition, oxidation state, or phase state. Assuming an SOA density of 1.06 g cm^{-3} , the SOA yield (0.10 to 0.99) is still higher for Cl-alkane oxidation as compared to OH-alkane oxidation. Molar SOA yields, calculated using the average molecular weight of species identified with the FIGAERO-CIMS, are summarized in Table S1.”

Anonymous Referee #2

(AR): Lines specified by the referee is copied below from the ACPD manuscript; revisions are noted in the author response

(1, RC) Wang et al. present results from environmental chamber experiments of C8-C12 alkane oxidation initiated by chlorine under dry/humid and high NO_x conditions. They show that yields are higher than for OH-initiated oxidation of the respective alkanes, indicative of the importance of these reactions for SOA production. Identified compounds include organonitrates, organochlorides. FIGAERO-CIMS data are used to look into the connection of chemistry and volatility via a new way of representing thermograms. Overall, this is a very well written paper, and the study and interpretation of results are sound. I therefore recommend this paper to be published after minor revisions. Apart from a few specific comments (see below), I have two general comments regarding the manuscript.

First, the manuscript would profit from a few more lines on its atmospheric relevance. Using alkanes as VOC precursors, and performing experiments under high NO_x conditions indicates the authors wanted to simulate an urban/polluted atmosphere. A short discussion on this, including the importance of Cl- oxidation in such environments, as well as the choice of RH conditions, would give the study more (atmospheric) importance.

(1, AR): We thank the referee for the recommendations. We have added some discussions on the experimental design choices and the atmospheric relevance of Cl oxidation chemistry

Revisions / Additions to Introduction:

P.2, L.26 – P.3, L.7: “ClNO₂ photolysis in the early morning produces Cl and NO_x, which has been shown to enhance RO₂ production from alkane oxidation in near coastal regions (Riedel et al., 2012) as well as OH radical propagation in urban environments (Young et al., 2014). In addition to reactive chlorine emissions from water treatment (Chang et al., 2001) and fuel combustion (Osthoff et al., 2008; Parrish et al., 2009), the rising usage of volatile chemical products (VCP) such as pesticides, cleaning products, and personal care products may be a significant source of reactive chlorine compounds and VOCs in urban environments (Khare and Gentner, 2018; McDonald et al., 2018). VOC-Cl oxidation products such as isomers of 1-chloro-3-methyl-3-butene-2- (CMBO), a tracer for isoprene-Cl chemistry (Nordmeyer et al., 1997), have been observed in highly polluted environments (Le Breton et al., 2018; Tanaka et al., 2003).”

Addition to Methods:

P.4, L.15 – 18: Under typical atmospheric conditions, elevated RH can be expected, especially within the marine boundary layer in near-coastal regions, where Cl-alkane chemistry may be important (Riedel et al., 2012). Therefore, SOA formation under humid conditions was also investigated.

Addition to Conclusion:

P.19, L.15 – 17: Overall, these results show that chlorine-alkane oxidation could be an important pathway for SOA production and ageing, especially in highly polluted environments replete with alkane, NO_x, and reactive chlorine emission sources.

(2, RC): Second, there is somewhat a disconnect in the narrative between section 3.1 and section 3.2, which also represents a disconnect between ACSM and FIGAERO-CIMS data. I suggest the authors try to connect these two parts better. Section 3.1 (SOA and organic chloride formation) is entirely ACSM based. Why? Why were FIGAERO-CIMS data not used? Some statements made in a tentative manner could be confirmed/ looked into using FIGAERO-CIMS data (see specific comments below).

(2, AR): The revised manuscript makes more use of quantitative FIGAERO-CIMS data, and compares ACSM to FIGAERO data. Additional gas- and particle-phase results are presented in the response to the following questions.

(3, RC): P. 1, l. 26/ p. 2 l. 11: Where is chlorine oxidation important? See comment above, the paper would benefit from a few more lines on its atmospheric relevance.

P.1 L.26: “Evaporation of POA due to dilution can provide additional gas-phase alkanes, which can undergo photooxidation initiated by OH, NO₃, as well as chlorine radicals (Aschmann and Atkinson, 1995; Atkinson and Arey, 2003).”

P.2 L.11: “Recent field studies have identified reactive chlorine compounds in diverse locales from natural and anthropogenic sources (Faxon and Allen, 2013; Finlayson-Pitts, 2010; Saiz-Lopez and von Glasow, 2012; Simpson et al., 2015).”

(3, AR): We have expanded the discussion on the conditions under which chlorine chemistry may be important as suggested as detailed in (1, AR).

(4, RC): P. 2, l. 32 –33: You specifically mention here low NO_x, as presumably the cited study was done under such. What are then the implications for your study? I suggest reformulating this sentence.

P.2. L.32-33: “Chlorine radicals can react with dihydrofuran via both H-abstraction and Cl-addition, producing chlorinated (e.g. dichlorotetrahydrofurans) and non-chlorinated compounds (e.g. furanones) under low NO_x conditions (Alwe et al., 2013).”

(4, AR): The referenced study was performed under low NO_x conditions. The main implication here is that the reaction between Cl and dihydrofuran can produce both chlorinated and non-chlorinated products. Under high NO_x conditions, both chlorinated and non-chlorinated organonitrate compounds may be formed. The following sentence has been added to clarify the implication of the NO_x study and its connection with the high NO_x scenario.

Addition to Introduction:

P.4, L.4 - 6: "...under low NO_x condition (Alwe et al. 2013). Similarly, formation of both chloronitrates (via Cl-addition) and organonitrates (via H-abstraction) from alkane-Chl oxidation is possible in the presence of NO_x."

(5, RC): P. 4, l. 28: UMR, why not HR? In Figure 5 you present molecular formulae of compounds, indicating HR analysis. Please clarify.

P.4, L.28: "The 2-D thermogram is comprised of normalized unit-mass resolution 1-D thermograms, each expressed as a percentage color scale of the maximum desorption signal."

(5, AR): We have conducted HR analysis and have experimented with a HR 2-D thermogram as the referee alluded to. We decided to present the UMR version due to its simplicity, where the multimodal thermal desorption behavior and a general T_{max}-molecular weight relationship can be visualized in the absence of explicit molecular formulae, which is especially helpful for studying the desorption behavior of high molecular weight compounds which may have a vast number of possible molecular makeups. Another practical concern with the HR 2-D thermogram is the uneven spacing of the molecular weight of the identified ions, which presents some technical issues for plotting on a heat map. We have added a brief discussion on the advantages and disadvantages of using UMR vs HR data for constructing the 2-D thermogram.

Change / Addition to Methods:

P.5, L.1 – 9: "The 2-D thermogram is comprised of normalized unit-mass resolution 1-D thermograms, each expressed as a percentage color scale of the maximum desorption signal. 2-D thermogram applications are discussed in Section 3.2. The advantage of using UMR over HR data is the ability to investigate the SOA thermal desorption behavior over the entire *m/z* and volatility (i.e. T_{max}) range without having to assign chemical formulae to all ion. This HR analysis is time-consuming especially for high molecular weight compounds whose exact molecular composition can be difficult to ascertain. The disadvantage of using UMR over HR data is the overlapping of ions and potential interference by isotopic signals or non-adduct ions. Therefore, the 2-D thermogram should be used as complement rather than a replacement of the HR analysis."

(6, RC): P. 5, l. 11: This could be confirmed with FIGAERO-CIMS data. Why were they not added?

P.5, L.11: "Given the same oxidation conditions, SOA products derived from longer alkane precursors appeared less oxidized..."

(6, AR): We have added Fig. 4(d) to support this observation using the FIGAERO-CIMS data, which shows that the SOA oxidation state decreases with increasing precursor length in agreement with the ACSM data analysis as shown in Table 1 and Fig. S1. Figure 4(b) in the ACPD manuscript is now Fig. 4(c).

Addition to Methods:

P. 7, L.8 – 16: “Based on the SOA molecular composition as observed by the FIGAERO-CIMS, the average oxidation state of carbon (OS_C) may be estimated,

$$OS_C = 2 \times O:C - H:C + NO_3:C + Cl:C \quad \text{Eq. (1)}$$

where $NO_3:C$, $Cl:C$, $O:C$, and $H:C$ are the molecular ratios of the number of $-NO_3$ functional groups, $-Cl$ functional groups, non- NO_3 oxygen atoms, and H atoms to the number of carbon atoms for any given compound. The average SOA OS_C is calculated based on iodide-adducts only. For simplicity, all organic ions were assumed to have equal sensitivity, which is known to vary with ion cluster binding energy and sample RH (Hyttinen et al., 2018; Iyer et al., 2016; Lopez-Hilfiker et al., 2016).”

Addition of Fig. 4(d):

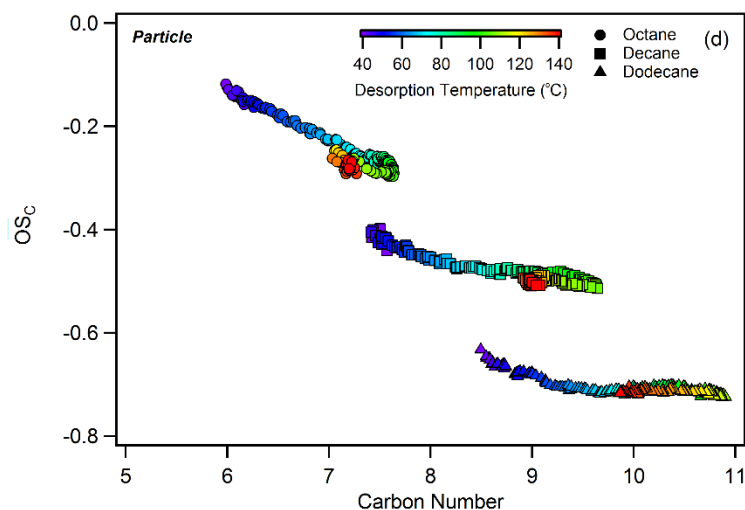


Figure 4d. Average oxidation state of carbon (OS_C) and carbon number of ions observed during the temperature-programmed desorption of SOA produced from the Cl-initiated oxidation of octane (Exp. 3), decane (Exp. 7), and dodecane (Exp. 11). Under similar oxidant conditions, SOA derived from longer VOC precursor were on average less oxidized.

(7, RC): P. 5, l. 18 – 19: I should cluster with Cl_2 . Why do you use the Cl^- signal to track Cl_2 ?

P.5, L.18-19: The Cl_2 concentration was estimated using I⁻ CIMS by tracking the Cl^- ion.

(7, AR): Cl^- ion was used at one point during the drafting of the manuscript. The Cl_2I^- ion was ultimately used in Fig. 1 shown in the discussion paper but the text was not updated by mistake. This has been corrected.

P.8, L.11 – 12: “The Cl_2 concentration was estimated using I⁻ CIMS by tracking the Cl_2I^- ion”

(8, RC): Please clarify. P. 5, l. 21 – 22: Did you see any evidence of that in FIGAERO-CIMS gas-phase measurements?

P.5, L.21-22: “Oxidation continued under UV driven by chlorine radicals, and the SOA concentration began to decay due to oxidative fragmentation (Kroll et al., 2011; Lambe et al., 2012; Wang and Hildebrandt Ruiz, 2017).”

(8, AR): We have added Fig. 4(b) to show the simultaneous increases in the average OS_C and decreases in the nc of gas-phase species as observed the I CIMS over the course of the photooxidation (0 to 60 mins), which are consistent with oxidative fragmentation. Results also show that octane oxidation products are significantly more oxidized compared to decane and dodecane oxidation products.

Addition of Fig. 4(b):

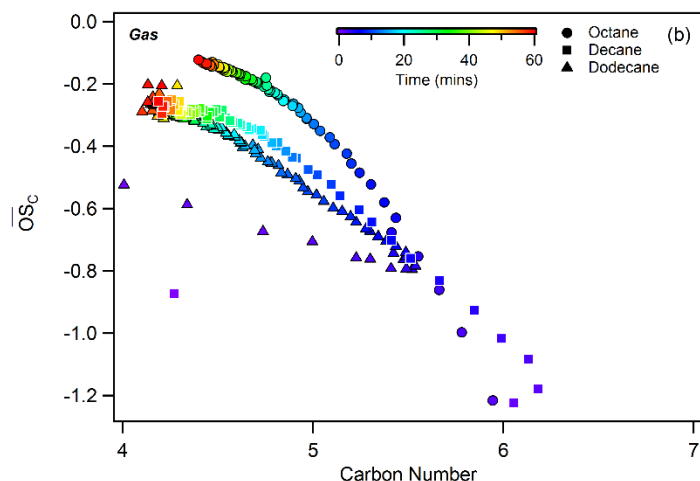


Figure 4(b). Average OS_C and nc of gas-phase compounds observed during the photooxidation period for Exp. 3 (Octane), 7 (decane), and 11 (dodecane). As oxidation continues, OS_C increased and nc decreased, consistent with oxidative fragmentation.

(9, RC): P. 6, l. 1-2: Can you confirm that with the organonitrate measurements of the FIGAEROCIMS?

P.6, L.1-2: “Higher initial NO concentrations led to higher SOA yields and lower ozone production for all precursors, as shown in Table 1 and Fig. S2. This is similar to alkane OH SOA formation, where higher NO concentrations lead to more abundant organic nitrate formation, which increases the SOA volume (Schilling Fahnstock et al., 2015) and density (Loza et al., 2014).”

(9, AR): FIGAERO data do show increased organonitrate abundance in the particle phase for SOA formed under NO-only conditions as compared to NO₂-only conditions in terms of both molar ratio (i.e. average number of -NO₃ functional group per molecule) and mass fraction (i.e. mass of organonitrate as a fraction of the identified SOA mass). For mixed NO-NO₂ conditions, the observed organonitrate molar ratio and mass fraction are closer to that observed under the NO₂ only condition. The results are incorporated into the main text. The tabulated data are added to the S.I.

Addition to Results and Discussion:

P.9, L.5 – 10: “[...] This is consistent with FIGAERO-CIMS results where the particulate organonitrate molar ratio (calculated as the average number of -NO₃ per molecule) and mass fraction were the highest in SOA produced under NO-only conditions (see Table S1). The organonitrate molar ratio also increased with the alkane precursor length, from 0.57-0.64 for

octane to 0.75-0.93 for dodecane. A similar trend was observed for the organonitrate mass fraction, which increased from 0.53-0.58 for octane to 0.66-0.72 for dodecane.”

(10, RC): P. 6, l. 16 – 18: *Also here the isotope signal should help you. Without that, the chloronitrate peak cannot be identified (based on Figure S8).*

P. 6, L. 16-18: “Compounds resembling chloronitrates (e.g. $\text{ONO}_2\text{C}_{12}\text{H}_{18}\text{ClO}_3\cdot\text{I}$ for dodecane) were tentatively identified in the particle-phase using the FIGAERO but they were not well separated from the shoulder of nearby organonitrate peaks (e.g. $\text{ONO}_2\text{C}_{12}\text{H}_{21}\text{O}_5\cdot\text{I}$), as shown in Fig. S8.”

(10, AR): As alluded to by the referee, ions containing Cl exhibit recognizable patterns (most notably at $m/z + 2$ positions), which was used to verify isolated organic chlorides and chloronitrates in this study. Well-isolated ions consistent with organic chloride, confirmed by the isotopic signals, were identified in the mass spectra. The difficulty with confirming (or denying) larger chloronitrates based on the isotopic signal is that non-chlorinated compounds dominate both the m/z and $m/z + 2$ positions. In this example, a C_{10} and a C_{11} organic nitrate compound could be fitted in place of the C_{12} chloronitrate. We now more strongly emphasize the uncertainties with organic chloride identification in the revised version of the manuscript, which was the intended purpose of the quoted text.

Change / Revision to S.I.:

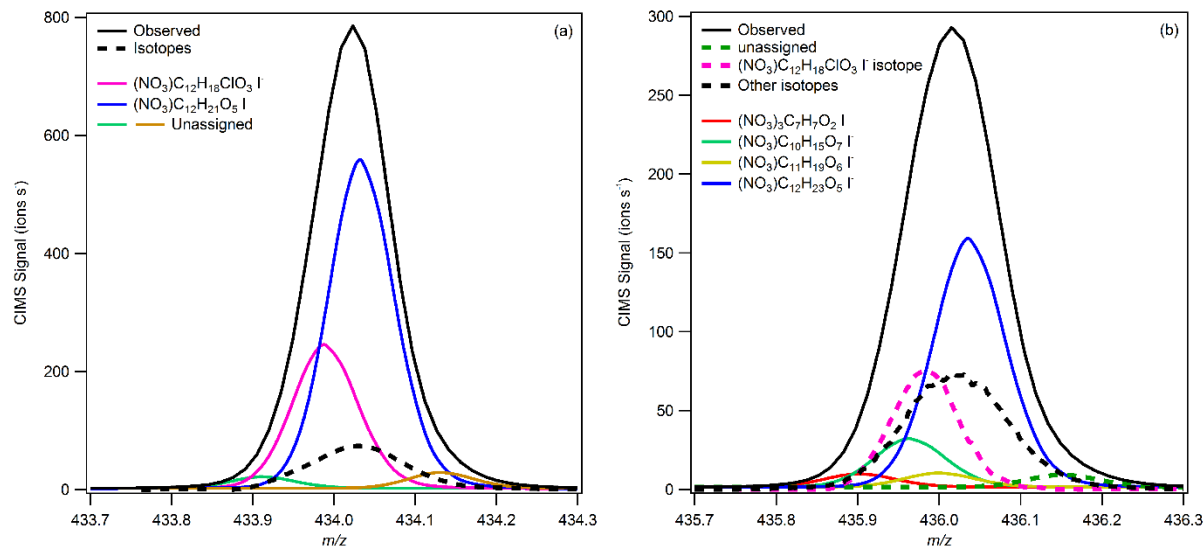


Figure S9: High resolution fitting at m/z (a) 434 and (b) 436 for FIGAERO-CIMS data from Exp. 11. The C_{12} chloronitrate ($\text{ONO}_2\text{-C}_{12}\text{H}_{18}\text{ClO}_3\cdot\text{I}$) peak is tentatively identified in (a) but it overlaps with the nearby stronger organonitrate ($\text{ONO}_2\text{-C}_{12}\text{H}_{21}\text{O}_5\cdot\text{I}$) peak. Because the chloronitrate peak is a weaker peak with significant overlap with a stronger peak, quantitative assessment would be challenging due to peak fitting uncertainties (Cubison and Jimenez, 2015). The presence of chloronitrate cannot be confirmed or rejected based on its unique isotopic signature at $m/z+2$ positions, as shown in (b), where nonchlorinated compounds also dominate.

(11, RC): P. 6, l. 21 – 22: Did you actually observe that as well if you compare your dry and humid experiments, no? You mention this as a finding in your conclusions as well, but I cannot find it as a result in the manuscript.

P.6, L.21-22: “Organochloride formation is expected to be lower under humid conditions, where DHF formation is inhibited (Holt et al., 2005; Zhang et al., 2014; Ziemann, 2011).

(11, AR): Based on data presented in the ACPD manuscript, evidence of organochloride suppression was observed for dodecane SOA (and to some extent the decane SOA), where the particulate chloride concentration (measured as HCl^+ ion in the ACSM) decreased from Exp. 11 (RH < 5 %) to Exp. 12 (RH ~67 %), as shown in Table 1. Using the FIGAERO-CIMS, we observed similar evidence for dodecane SOA in the terms of the mass fraction of -Cl functional group and the overall mass fraction of organic chlorides and chloronitrates. For octane and decane SOA, no clear evidence was observed. We have clarified this in the main text and added the results obtained using FIGAERO-CIMS.

Addition to Results and Discussion:

P.10, L.18 – 26: “[...]Evidence consistent with organochloride suppression under humid condition was observed for dodecane SOA only, where the organochloride (including chloronitrates) mass fraction decreased from 0.15 (Exp. 11, < 5 % RH) to 0.13 (Exp. 12, 67 % RH) as measured by the FIGAERO-CIMS. The mass fraction of the -Cl functional group decreased from 1.8 E^{-2} to 1.6 E^{-2} as measured by the FIGAERO-CIMS (Table S1) or from 1.4 E^{-2} to 1.1 E^{-2} as measured by the ACSM (Table 1) as the RH increased. No clear differences were observed for octane or decane SOA, which may be due to the less extreme RH conditions investigated, uncertainties with organochloride ion identification in the CIMS, or the lower organochloride concentrations observed in Exps.1-8, which is especially challenging for chloride quantification using the ACSM.”

(12, RC): P. 7, l. 3-4: Are those fragmentation reactions in the particle phase, with subsequent evaporation of the resulting compounds? This would be consistent with the observation of loss of SOA mass (mentioned e.g. on p. 5, l. 21 – 22). Please elaborate. Experiments shown here are all under dry conditions. What about humid conditions?

P.7, L.3-4: “As oxidation continued, the importance of fragmentation reactions increased relative to that of functionalization reactions (Lambe et al., 2012).”

P. 5, L. 21-22: “Oxidation continued under UV driven by chlorine radicals, and the SOA concentration began to decay due to oxidative fragmentation (Kroll et al., 2011; Lambe et al., 2012; Wang and Hildebrandt Ruiz, 2017).”

(12, AR): We would expect the oxidation and fragmentation to occur primarily in the gas-phase, resulting in the change of particle-phase composition via equilibrium partitioning. Previous study with OH-initiated pentadecane (C_{15}) shows that gas-phase chemistry drives oxidation (aided by the dehydration of cyclic hemiacetal, which does occur in the condensed phase), while heterogeneous reactions (e.g. hemiacetal formation) would decrease the aerosol volatility. Heterogeneous oxidation of organic and inorganic aerosol has been reported to occur at non-

negligible rates (Bertram et al., 2001; George and Abbatt, 2010) but is beyond the scope of this work. SOA decay was also observed under humid conditions. We note that vapor wall loss, which can worsen under more humid conditions (Huang et al., 2018b), would also contribute to the observed SOA concentration decrease in addition to oxidative fragmentation. This has been clarified in the manuscript.

Revision/Addition to Results and Discussion:

P.11, L.18 – 23: “As oxidation continued, driven primarily by gas-phase chemistry (Aimant and Ziemann, 2013), the importance of fragmentation reactions increased relative to that of functionalization reactions (Lambe et al., 2012). The heterogeneous oxidation of SOA (Bertram et al., 2001; George and Abbatt, 2010), which is expected to drive the oxidation of very large ($n > 30$) alkanes (Lim and Ziemann, 2009b), may also contribute to oxidation and fragmentation observed here, but its impacts are beyond the scope of this work.”

(13, RC): P. 7, l. 13 – 14: It becomes clear after discussion of Figure 5, but it would be helpful for the reader to mention here why you use the temperature range of 40–140 oC

P.7, L.13-14: “The spectra are calculated from the average desorption ion signals observed when the filter temperature was between 40 and 140 oC.”

(13, AR): This has been clarified in the revised manuscript.

Addition to Results and Discussion:

P.12, L.6 – 9: “[...] As shown below and in Fig. 5, SOA components desorbed mostly effectively in this temperature range, with most organic ions having T_{\max} within this temperature range. At desorption temperature above 140 °C, inorganic ions began to dominate the spectra.”

(14, RC): P. 8, l. 8 – 10: What do you base your interpretation of “low-temperature thermal fragmentation products” on? I agree that there must be fragmentation, but I am not sure you have enough evidence for that being thermal fragmentation during desorption.

P.8 L.8-10: “These small organic compounds (detected as I- adducts) were likely low-temperature thermal fragmentation products. Prominence of ions smaller than m/z 127 (i.e. ions generated not from iodide-adduct formation but possibly acid exchange or charge transfer), including Cl- and a range of organic ions, was consistent with low-temperature thermal fragmentation.”

(14, AR): Perhaps the term “low-temperature decomposition products” is more appropriate than “low-temperature fragmentation products” in this context. We recognize that some compounds in region 1 (Fig. 5) may correspond to semi-volatile molecular compounds. At the same time, there are compounds detected that would be too volatile to be present in the particle-phase and should therefore be some form of instrument artifact. Because their intensity varied with the desorption temperature (hence the apparent T_{\max}), they should be thermally induced, which led to the designation of “low-temperature decomposition products.” We have clarified this description.

Revision to Results and Discussion:

P.13, L14 – 21: “Region 1 ($m/z < 350$, $40 < T_{\max} < 90$ °C) was composed of a group of semi-volatile compounds with similar T_{\max} values. This region also includes iodide-adducts which correspond to species that are too volatile to be present as molecular compounds in the particle phase and are likely low-temperature decomposition products. Prominence of ions smaller than m/z 127 including Cl^- and a range of organic ions, could be acid exchange or charge transfer products (as opposed to I^- adducts) of low-temperature decomposition products.”

(15, RC): P.9, section 3.3: How reproducible are your thermograms and corresponding T_{\max} for one compound and stable conditions? This information should be added e.g. to the supplementary section.

P.9, section 3.3: (summary) T_{\max} was observed to increase with ammonium sulfate loading for ammonium sulfate decomposition ions. Similar loading dependence was observed for some SOA components for filters collected at different points during an experiment over various durations.

(15, AR): The thermogram reproducibility is validated using aerosols (injected into the chamber) generated from a nebulized $1.2 \text{ E}^{-2} \text{ M}$ levoglucosan aqueous solution. The results are shown in the updated Fig. 6. The thermogram shape is fairly reproducible as shown in Fig. 6(a). Similar to observations made for ammonium sulfate particles (now Fig. S7), the T_{\max} for levoglucosan aerosol also increases with filter loading. A sigmoidal fitting curve is shown to guide the eyes. T_{\max} appears to level off towards the higher filter loading range, possibly due to saturation effects (Huang et al., 2018a).

Update of Fig. 6

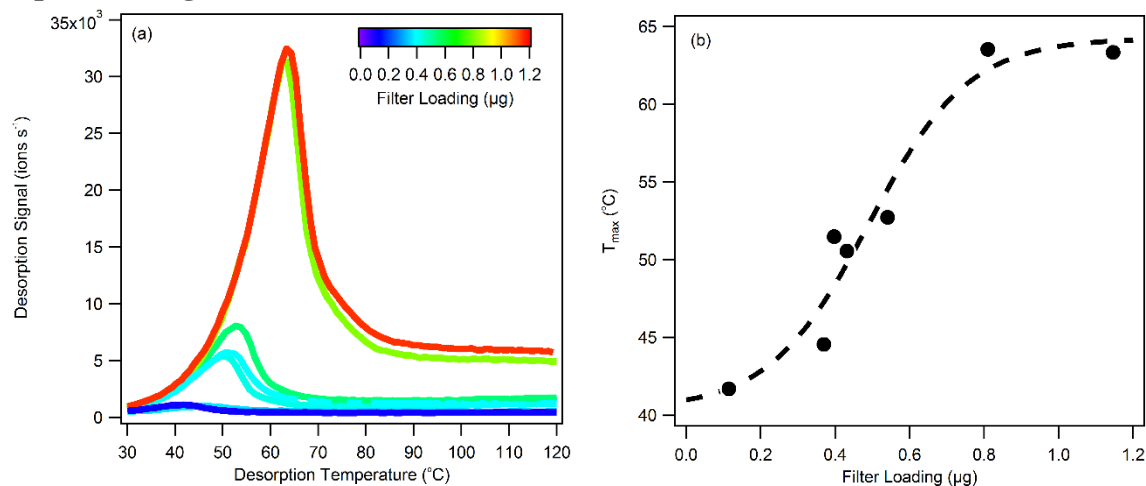


Fig. 6: (a) The 1-D thermograms for levoglucosan ($\text{C}_6\text{H}_{10}\text{O}_5$) at different loading conditions and (b) the correlation between filter loading and T_{\max} . Levoglucosan aerosol was generated by nebulizing a $1.2 \text{ E}^{-2} \text{ M}$ aqueous solution. The aerosol was injected into the clean Teflon chamber, collected onto the FIGAERO filter, and analyzed. The T_{\max} -loading correlation for pure levoglucosan could be described by a sigmoid function, leveling off at 41 and 65 °C under very low and very high loading conditions, respectively.

(16, RC): P. 11, l. 22 – 23: This sentence is formulated too strongly based on the observations you present in your results section.

P.11, L.22-23: “Using the ACSM and the FIGAERO-CIMS, trace amounts of alkane-derived organochlorides were observed, produced via chlorine-addition to the heterogeneously produced dihydrofuran compounds.”

(16, AR): We have revised the conclusion slightly to reflect the uncertainties with organochloride identification.

Revision to Conclusion:

P.19, L.9 – 11: “Trace amounts of alkane-derived organochlorides were observed using the ACSM and the FIGAERO-CIMS, likely produced via chlorine-addition to the heterogeneously produced dihydrofuran compounds.”

(17, RC): Technical corrections: P. 6, l. 8: Should be ACSM P. 8, l. 3: Propose

(17, AR): Technical errors have been corrected.

Chlorine-initiated oxidation of n-alkanes under high NO_x conditions: Insights into secondary organic aerosol composition and volatility using a FIGAERO-CIMS

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Abstract. Chlorine-initiated oxidation of *n*-alkanes (C₈₋₁₂) under high nitrogen oxides conditions was investigated. Observed secondary organic aerosol yields (0.16 to 1.65) are higher than those for OH-initiated oxidation of C₈₋₁₂ alkanes (0.04 to 0.35). A High-Resolution Time-of-Flight Chemical Ionization
10 Mass Spectrometer coupled to a Filter Inlet for Gases and AEROSols (FIGAERO-CIMS) was used to characterize the gas- and particle-phase molecular composition. Chlorinated organics were observed, which likely originated from chlorine addition to the double bond present on the heterogeneously produced dihydrofurans. A two-dimensional thermogram representation was developed to visualize composition and relative volatility of organic aerosol components using unit-mass resolution data.
15 Evidence of oligomer formation, ~~thermal fragmentation~~ and thermal decomposition was observed. Aerosol yield and oligomer formation were suppressed under humid conditions (35 to 67 % RH) relative to dry conditions (under 5 % RH). The temperature at peak desorption signal, T_{max}, a proxy for aerosol volatility, was shown to change with aerosol filter loading, which should be constrained when evaluating aerosol volatilities using the FIGAERO-CIMS. Results suggest that long-chain anthropogenic alkanes
20 could contribute significantly to ambient aerosol loading over their atmospheric lifetime.

1 Introduction

Alkanes account for up to 90% of all anthropogenic hydrocarbon emissions and 12 % (140 Tg yr⁻¹) of annual non-methane hydrocarbon emissions (Fraser et al., 1997; Goldstein and Galbally, 2007; Guenther et al., 2012; Rogge et al., 1993; Schauer et al., 1999, 2002). Linear, branched, cyclic alkanes, and
25 aromatics are major components of gasoline, diesel, motor oil, and other petroleum products (Caravaggio

et al., 2007; Kleeman et al., 2008; Schauer et al., 1999). Depending on its vapor pressure, the alkane can be emitted as volatile organic compound (VOC), intermediate-volatility organic compound (IVOC), semi-volatile organic compound (SVOC), or primary organic aerosol (POA). Evaporation of POA due to dilution can provide additional gas-phase alkanes, which can undergo photooxidation initiated by OH, NO₃, as well as chlorine radicals (Aschmann and Atkinson, 1995; Atkinson and Arey, 2003). Consequently, alkanes can have significant contributions to SOA production in urban environments (Dunmore et al., 2015). Hydrocarbon-like organic aerosol, which is often associated with POA and alkane oxidation, contributes on average 36 % to fine particulate matter (PM₁) in urban environments (Zhang et al., 2007). Influences of alkane emission and oxidation on SOA formation can be observed in remote regions as well (Carlton et al., 2010; Chrit et al., 2017; Hoyle et al., 2011; Minguillón et al., 2011, 2016; Patokoski et al., 2014; Saito et al., 2004; Sartelet et al., 2012). Alkane emissions can be sporadic and scattered, complicating both monitoring and modeling efforts (Lyon et al., 2015; Zavala-Araiza et al., 2015, 2017). Using laboratory results on OH-initiated SOA formation from alkanes under low- and high-NO_x conditions (Jordan et al., 2008; Lamkaddam et al., 2017; Lim and Ziemann, 2009a, 2005, 2009b; Loza et al., 2014; Presto et al., 2009, 2010; Schilling Fahnstock et al., 2015; Takekawa et al., 2003; Tkacik et al., 2012; Yee et al., 2012, 2013; Zhang et al., 2014), model predictions for OA concentrations can be improved, though the predicted OA is often less oxidized than observed (Bahreini et al., 2012; DeCarlo et al., 2010; Dzepina et al., 2009; de Gouw et al., 2011; Murphy and Pandis, 2009; Shrivastava et al., 2008; Zhang et al., 2007), which could point to missing oxidants (e.g. ~~ehlorine-Cl~~radicals) and SOA oxidation mechanisms in the models (Murphy and Pandis, 2009).

Recent field studies have identified reactive chlorine compounds in diverse locales from natural and anthropogenic sources (Faxon and Allen, 2013; Finlayson-Pitts, 2010; Saiz-Lopez and von Glasow, 2012; Simpson et al., 2015). Tropospheric chlorine chemistry can enhance ozone production (Tanaka et al., 2003). Nighttime production of nitryl chloride mediated by heterogeneous uptake of NO_x onto chloride-containing particles represents an ubiquitous source ~~offer~~ reactive chlorine (Thornton et al., 2010). In addition ~~to nighttime chemistry~~, biomass burning could also act as a source of ClNO₂ (Ahern et al., 2018). ClNO₂ photolysis in the early morning produces Cl^{*} and NO_x, which has been shown to enhance RO₂ production from alkane oxidation in near coastal regions (Riedel et al., 2012) as well as OH radical

propagation in urban environments (Young et al., 2014). In addition to reactive chlorine emissions from water treatment (Chang et al., 2001) and fuel combustion (Osthoff et al., 2008; Parrish et al., 2009), the rising usage of volatile chemical products (VCP) such as pesticides, cleaning products, and personal care products may be a significant source of reactive chlorine compounds and VOCs in urban environments (Khare and Gentner, 2018; McDonald et al., 2018). VOC--Cl oxidation products such as isomers of 1-chloro-3-methyl-3-butene-2- (CMBO), a tracer for isoprene-Cl chemistry (Nordmeyer et al., 1997), have been observed in highly polluted environments (Le Breton et al., 2018; Tanaka et al., 2003). ClNO₂ photolysis can dominate RO₂ radical production in the early morning (Riedel et al., 2012).

Akin to hydroxyl-OH radicals, chlorine-Cl radicals initiate reactions with alkanes via hydrogen-abstraction, forming hydrogen chloride (HCl) and alkylperoxy radicals (RO₂). According to structure-activity relationships, terminal hydrogen abstraction occurs more frequently with alkane-Cl than with alkane-OH reactions (Kwok and Atkinson, 1995), resulting in different product distributions; for example, increased formation of primary alkyl nitrates. The bimolecular gas-phase reaction rate constants with linear alkanes for hydroxylOH radicals and chlorine-Cl radicals increase with the alkane chain length. Consequently, the reaction rate constants for chlorine-Cl and linear C₈₋₁₂ alkanes range from 4.05 × 10⁻¹⁰ (octane) to 5.36 × 10⁻¹⁰ cm⁻³ molecules⁻¹ s⁻¹ (dodecane) at 298 K and 1 atm (Aschmann and Atkinson, 1995), which is over an order of magnitude higher than the rate constants for hydroxyl-OH radicals, 8.11 × 10⁻¹² (octane) to 1.32 × 10⁻¹¹ cm⁻³ molecules⁻¹ s⁻¹ (dodecane; Atkinson and Arey, 2003). Studies show that chlorineCl-initiated oxidation of volatile organic compounds such as isoprene, monoterpenes, toluene, and polycyclic aromatic hydrocarbons can lead to rapid SOA formation with high yields (Cai et al., 2008; Cai and Griffin, 2006; Huang et al., 2014; Karlsson et al., 2001; Ofner et al., 2013; Riva et al., 2015; Wang and Hildebrandt Ruiz, 2017). Compounds consistent with isoprene-derived organochloride were recently observed in filter samples collected in Beijing (Le Breton et al., 2018).

Although all initial C₈₋₁₂ alkane-Cl oxidation products are expected to be non-chlorinated, formation of alkane-derived organochlorides is possible from chlorine-Cl addition to ~~the~~ multi-generational products. Studies show that the oxidation of alkanes with 5 or more linear carbons produces 1,4-hydroxycarbonyl that can undergo a rate-limiting, acid-catalyzed heterogeneous reaction to produce dihydrofuran (DHF) compounds (Atkinson et al., 2008; Holt et al., 2005; Jordan et al., 2008; Lim and Ziemann, 2009b, 2009c).

DHF is highly reactive: For 2,5-dihydrofuran, the bimolecular reaction rate constants with O₃, OH and Cl are $1.65 \pm 0.31 \times 10^{-17}$, $6.45 \pm 1.69 \times 10^{-11}$, and $4.48 \pm 0.59 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively (Alwe et al., 2013, 2014). Chlorine radicals can react with dihydrofuran via both H-abstraction and Cl-addition, producing chlorinated (e.g. dichlorotetrahydrofurans) and non-chlorinated compounds (e.g. furanones) under low NO_x conditions (Alwe et al., 2013). Similarly, formation of both chloronitrates (via Cl-addition) and organonitrates (via H-abstraction) from alkane-Cl oxidation is possible in the presence of NO_x.

In this study, environmental chamber studies were conducted using long-chain (C₈₋₁₂) *n*-alkanes and ~~ehlorine~~Cl radicals under high NO_x conditions to evaluate the ~~ehlorine~~Cl-initiated SOA formation from alkanes and to characterize the molecular composition of gas and aerosol compounds.

2 Methods

2.1 Environmental chamber experiments and instrumentation

Experiments were conducted inside a 10 m³ Teflon[®] chamber at 298 K, using UV lights to generate radicals. The NO₂ photolysis rate was measured to characterize the UV intensity (Carter et al., 2005) and was found to be similar to ambient levels (0.53 min^{-1} at 0° zenith angle) at approximately 0.5 min^{-1} . The chamber relative humidity (RH) ranged from 0 to 67 %. For dry experiments, the chamber was filled with dried clean air supplied by a clean air generator (model 737R, Aadco). Under typical atmospheric conditions, elevated RH can be expected, especially within the marine boundary layer in near-coastal regions, where Cl-alkane chemistry may be important (Riedel et al., 2012). Therefore, SOA formation under humid conditions was also investigated. For humid experiments (i.e. RH > 20 %), the chamber was flushed overnight with humidified clean air. To reduce wall-loss, dried ammonium sulfate seed particles were injected into the chamber. The seed particles were generated from a 0.01 M aqueous ammonium sulfate solution using an aerosol generation system (AGS 2002, Brechtel). Chlorine gas (101 ppm in N₂, Airgas) was injected as the ~~ehlorine~~Cl radical precursor. Each *n*-alkane (*n*-octane, 99 %; *n*-decane, 99 %; dodecane > 99%, Sigma-Aldrich) was first injected into a glass gas sampling tube (Kimble-Chase, 250 mL), which was flushed with gently heated clean air into the chamber at 2 lpm for at least 30 minutes.

Precursor NO (9.98 ppm in N₂, Airgas) and NO₂ (9.86 ppm in N₂, Airgas) were injected into the chamber using a mass flow controller (GFC17, Aalborg). Initial concentrations of VOC and oxidant precursors are summarized in Table 1. Gas-phase NO and NO₂ concentrations were monitored by a chemiluminescence monitor (200E, Teledyne). The O₃ concentration was monitored using a photometric ozone analyzer (400E, Teledyne). The start of photooxidation, initiated by turning on all the UV lights after the precursors were well-mixed in the chamber, was designated as the reference point (i.e. time 0 min) for each experiment. UV lights were turned off after 60 minutes. On the day before and after each SOA formation experiment, ammonium sulfate seed particles and 50 ppb of chlorine gas were injected into the chamber. UV lights were turned on to generate ~~chlorine-Cl~~ radicals and remove residual reactive organic compounds in the chamber. Minimal SOA formation was observed during these cleaning experiments.

Particle size distributions were characterized using a scanning electrical mobility system (SEMS, Brechtel model 2002). The particle-phase bulk chemical composition was measured using an aerosol chemical speciation monitor (ACSM, Aerodyne). The ACSM was calibrated with 300nm size-selected ammonium nitrate and ammonium sulfate aerosols generated from nebulized 0.005 M solutions using the AGS to determine the nitrate response factor (RF) and relative ionization efficiencies (RIE) for ammonium and sulfate, which are required for ion-to-mass signal conversions. Using electron impact ionization, the ACSM can measure the submicron, non-refractory aerosol bulk composition at one minute intervals (Budisulistiorini et al., 2013; Ng et al., 2011a). Using a standard fragmentation table (Allan et al., 2004), the ACSM can speciate the aerosol content into organics, nitrate, sulfate, ammonium, and chloride (Ng et al., 2011a). The ability of the ACSM to detect organic chloride using HCl⁺ (*m/z* 36) has been demonstrated previously for isoprene-Cl SOA (Wang and Hildebrandt Ruiz, 2017). The default RIE_{chl} value of 1.3 was used for chloride mass conversion. The Cl⁺ (*m/z* 35) ion was excluded from chlorine quantification as it showed inconsistent response to non-refractory chlorides (e.g. ammonium chloride). ACSM data were analyzed in Igor Pro V6.37 (Wavemetrics, Inc.) using ACSM local v1603 (Aerodyne) and other custom routines. AOrganic aerosol concentrations were calculated using ACSM measurements assuming a collection efficiency of 0.5 and RIE of 1.4, s-were corrected for depositional particle wall loss (Pathak et al., 2007) but not for organic vapor loss (Huang et al., 2018b; Krechmer et al., 2017; Nah et al., 2017).

2.2 FIGAERO-CIMS

A high-resolution time-of-flight chemical ionization mass spectrometer (CIMS, Aerodyne) was used to measure the gas-phase chemical composition using I⁻ as the chemical ionization reagent. Humidified UHP N₂ was flushed over a methyl iodide permeation tube and then through a ²¹⁰Po ionizer into the ion-molecule reaction (IMR) chamber of the CIMS. Theory and operation of the CIMS are described in detail elsewhere (Aljawhary et al., 2013; Bertram et al., 2011; Lee et al., 2014; Wang and Hildebrandt Ruiz, 2017). The CIMS inlet ~~was~~ coupled to a filter inlet for gases and aerosols (FIGAERO), which has been used in a number of studies to investigate the chemical composition and volatility of particle-phase compounds (D'Ambro et al., 2017; Gaston et al., 2016; Huang et al., 2018a; Lee et al., 2016; Lopez-Hilfiker et al., 2014, 2015; Stark et al., 2017; Thompson et al., 2017). The FIGAERO system alternated between two operational modes. In the aerosol collection mode, ~~a~~ gas-aerosol mixture was drawn through a PTFE filter (Zefluor[®] 2.0 μm 24mm, Pall Corp.) at 3 SLPM for 15 to 45 minutes while gas species were sampled and analyzed. In the desorption mode, clean air or UHP N₂ was passed through the filter and heated to 200 °C (measured just above the filter) at a rate of ~~approximately~~ 5 to 10 °C min⁻¹ for 40 to 20 minutes, respectively. The filter was then soaked at 200 °C for 20 minutes. The volatilized vapor was sampled by the CIMS, and the desorption signal as a function of temperature can be used to construct a one-dimensional (1-D) thermogram (e.g. Fig. 6a). For a monomeric compound, the desorption signal as a function of temperature is expected to be monomodal (Lopez-Hilfiker et al., 2014). The temperature at the peak desorption signal, T_{max} correlates with the enthalpy of sublimation (dH_{sub}) and the saturation vapor pressure (C*) of the compound (Lopez-Hilfiker et al., 2014, 2015). However, some compounds may exhibit bimodal or multimodal behavior, with a second desorption mode occurring at much higher temperatures than expected, which is often interpreted as the result of thermal ~~fragmentation or~~ decomposition of larger oligomeric compounds (Huang et al., 2018a; Lopez-Hilfiker et al., 2014; Stark et al., 2017; Wang et al., 2016).

CIMS and FIGAERO data analysis was conducted in Igor Pro with Tofware v2.5.10 (Tofwerk) and custom routines. Hundreds of ions belonging to diverse chemical families can be retrieved from the mass spectra. To simultaneously represent the chemical composition, relative aerosol volatility (i.e. T_{max} distribution), and multimodal thermal desorption behaviors, a two-dimensional (2-D) thermogram

framework was developed. The 2-D thermogram is comprised of normalized unit-mass resolution 1-D thermograms, each expressed as a percentage color scale of the maximum desorption signal. 2-D thermogram ~~development and~~ applications are discussed ~~in detail~~ in Section 3.2. The advantage of using UMR over HR data is the ability to investigate the SOA thermal desorption behavior over the entire m/z and volatility (i.e. T_{\max}) range without having to assign chemical formulae to all ion. This HR analysis is time-consuming especially for high molecular weight compounds whose exact molecular composition can be difficult to ascertain. The disadvantage of using UMR over HR data is the overlapping of ions and potential interference by isotopic signals or non-adduct ions. Therefore, the 2-D thermogram should be used as complement rather than a replacement of the HR analysis. Based on the SOA molecular composition as observed by the FIGAERO-CIMS, the average oxidation state of carbon (OS_C) may be estimated.

$$OS_C = 2 \times O:C - H:C + NO_3:C + Cl:C \quad \text{Eq. (1)}$$

where $NO_3:C$, $Cl:C$, $O:C$, and $H:C$ are the molecular ratios of the number of $-NO_3$ functional groups, $-Cl$ functional groups, non- NO_3 oxygen atoms, and H atoms to the number of carbon atoms for any given compound. The average SOA OS_C is calculated based on iodide-adducts only. For simplicity, all organic ions were assumed to have equal sensitivity, which is known to vary with ion cluster binding energy and sample RH (Hytinen et al., 2018; Iyer et al., 2016; Lopez-Hilfiker et al., 2016).

3 Results and Discussion

3.1 SOA and organic chloride formation

Experimental conditions and results are summarized in Table 1. Chlorine-alkane SOA yields increased with VOC precursor length, consistent with the trend observed for OH-alkane SOA (Jordan et al., 2008; Lim and Ziemann, 2009b; Presto et al., 2010; Schilling Fahnstock et al., 2015; Yee et al., 2012, 2013). For similarly functionalized alkane oxidation products, the vapor pressure decreases roughly log-linearly as the precursor carbon number increases from 8 to 15 (Jordan et al., 2008; Presto et al., 2010). Comparison of the unit-mass ACSM spectra for octane (Exp. 3), decane (Exp. 7), and dodecane (Exp. 11) SOA in Fig. S1 shows a consistent increase in the fractional contributions to the bulk OA mass (i.e. $f_{m/z}$)

by organic ions at m/z 27 ($C_2H_3^+$), 41 ($C_3H_5^+$), 55 ($C_4H_7^+$) and 57 ($C_4H_9^+$) with increasing alkane length. Select odd m/z ions, noticeably m/z 55 and 57, have been used as tracers for hydrocarbon-like organic aerosol (HOA), and sometimes for primary aerosol emissions as well (Ng et al., 2011b; Ulbrich et al., 2009). Given the same oxidation conditions, SOA products derived from longer alkane precursors appeared less oxidized, as seen by the decrease in f_{44} (presumably mostly CO_2^+), but more hydrocarbon-like, as seen by the increase in $f_{57/55}$, consistent with previous observations (Lambe et al., 2012; Loza et al., 2014). The results are summarized in Table 1. As the alkane chain length increases, the increased SOA production also favors the partitioning of semi-volatile compounds into the particle-phase (Donahue et al., 2006; Pankow, 1994), further lowering f_{44} .

Time series of gas-phase NO, NO₂, O₃, Cl₂, and suspended particle-phase organics and chlorine concentrations during photooxidation are shown in Fig. 1 using dodecane-Cl oxidation under low RH (Exp. 11) as the representative example. ~~The Cl₂ concentration was estimated using I-CIMS by tracking the Cl-NO concentration decreased sharply at the beginning of the experiment accompanied by rapid ozone production and increases in NO₂ concentration.~~ The Cl₂ concentration was estimated using I-CIMS by tracking the Cl₂I⁻ ion. In addition, ions consistent with HO₂NO₂, HONO, and ClNO₂ were observed in the gas phase, as shown in Fig. 1. The ClNO₂I⁻ ions are expected to correspond to both ClNO₂ (< 20 %) and chlorine nitrite (ClONO, > 80 %) from the reaction between Cl[•] and NO₂ (Golden, 2007; Niki et al., 1978). Formation of HO₂NO₂ from the reaction of HO₂ and NO₂ has been observed using I-CIMS previously (Veres et al., 2015). Formation of HONO was likely due to the interactions between HO_x and NO (see R. S2 and R. S3 in the SI). Under UV, HONO decays to background level. Production of HO₂NO₂ and HONO is indicative of secondary HO_x chemistry enabled by primary Cl-alkane oxidation chemistry, consistent with previous studies (Wang and Hildebrandt Ruiz, 2017; Young et al., 2014).

The NO concentration decreased sharply at the beginning of the photooxidation accompanied by increases in the concentrations of NO₂ and ozone. SOA production was most rapid during this initial period (0 to 10 min). Afterwards, at around 15 min in Fig. 1, the concentrations of NO₂ and ozone stabilized. Oxidation continued under UV driven by ~~chlorine-Cl~~ radicals, and the SOA concentration began to decay due to oxidative fragmentation (Kroll et al., 2011; Lambe et al., 2012; Wang and Hildebrandt Ruiz, 2017) and wall loss. ~~The ozone~~ Ozone production continued slowly under UV at ~0.24

ppb min⁻¹. Slight NO₂ production (< 0.1 ppb min⁻¹) was also observed, which may be due to production of nitrous acid (HONO) on the Teflon[®] surface, a common background contaminant in environmental chambers (Carter et al., 2005; Rohrer et al., 2004). ~~Particulate nitrate (NO₃) followed the bulk organics trend and the ratios of NO₃ to organic mass are summarized in Table 1. The NO₃ to organics ratio did not change significantly for different alkane precursors, likely because the gas-phase oxidation chemistry is similar for C₈ to C₁₇ alkanes (Jordan et al., 2008). The branching ratio for RO₂ + NO reaction increases only slightly from C₈ (0.24) to C₁₂ (0.29), plateauing after C₁₃ for OH initiated oxidations (Arey et al., 2001; Atkinson et al., 1983; Yeh and Ziemann, 2015). The decrease in NO₃ to organics ratio from decane Cl SOA (0.12-0.13) to dodecane Cl SOA (0.08-0.11) is consistent with partitioning of more volatile, less oxidized compounds into the particle phase under higher SOA loading conditions. The~~

SOA production was dependent on the initial NO and NO₂ concentrations, as shown in Fig. S2. ~~In all experiments, NO decayed to zero in the first 10 minutes of the experiment, during which time most of the SOA formation occurred.~~ Higher initial NO concentrations led to higher SOA yields and lower ozone production for all precursors, as shown in Table 1 and Fig. S2. This is similar to alkane-OH SOA formation, where higher NO concentrations lead to more abundant organic nitrate formation, which increases the SOA volume (Schilling Fahnstock et al., 2015) and density (Loza et al., 2014). This is consistent with FIGAERO-CIMS results where the particulate organonitrate molar ratio (calculated as the average number of -NO₃ per molecule) and mass fraction were the highest in SOA produced under NO-only conditions (see Table S1). The organonitrate molar ratio also increased with the alkane precursor length, from 0.57-0.64 for octane to 0.75-0.93 for dodecane. A similar trend was observed for the organonitrate mass fraction, which increased from 0.53-0.58 for octane to 0.66-0.72 for dodecane. -The alkane-Cl SOA yields, ranging from 0.16 (octane) to 1.65 (dodecane), are 4 times higher than the alkane-OH SOA yields (0.04 for octane and 0.35 for dodecane) that were obtained using 1 ppm alkane, 10 ppm methyl nitrite, and 10 ppm NO (Lim and Ziemann, 2009a), much higher than the precursor concentrations used here (13 to 15 ppb alkanes, < 40 ppb NO_x, 40 ppb Cl₂). Formation of primary alkyl nitrates, due to terminal H-abstraction by Cl could contribute to the higher SOA yields observed for alkane-Cl than for alkane-OH oxidation, as primary alkyl nitrates have lower saturation vapor pressures than secondary alkyl nitrates (Lim and Ziemann, 2009b; Yeh and Ziemann, 2014, 2015). The apparent

SOA density, calculated using the ACSM SOA mass measurement and the SEMS SOA volume measurement, was $2.1 \pm 0.3 \text{ g cm}^{-3}$, which is substantially higher than that reported for OH-alkane SOA formed under high NO_x conditions, 1.06 to 1.28 g cm^{-3} (Lim and Ziemann, 2009a; Loza et al., 2014). These differences could be due to uncertainties associated with the ACSM and similar instruments, specifically the RIE (Li et al., 2018; Xu et al., 2018) and CE (Docherty et al., 2013; Middlebrook et al., 2012; Robinson et al., 2017), which may vary with SOA composition, oxidation state, or phase state. Assuming an SOA density of 1.06 g cm^{-3} , the SOA yield (0.10 to 0.99) is still higher for Cl-alkane oxidation as compared to OH-alkane oxidation. Molar SOA yields, calculated using the average molecular weight of species identified with the FIGAERO-CIMS, are summarized in Table S1.

Although the initial Cl-alkane reactions proceed via a H-abstraction pathway, particulate chlorine was observed using the ~~ACMS-ACSM~~ as shown in Fig. 1. Direct halogenation of the C_{8-12} alkyl radicals is expected to be minimal, given the low amounts of Cl_2 present (maximum of 40 ppb). A carbon-carbon double bond is required to enable ~~Cl-chlorine~~-addition reactions and organic chlorine formation. The heterogeneous production of dihydrofuran (DHF) via 1,4-hydroxycarbonyl uptake, acid-catalyzed isomerization, and dehydration reactions (Atkinson et al., 2008; Jordan et al., 2008; Lim and Ziemann, 2009c, 2009b), followed by Cl addition to the DHF double bond, could be the source of observed organic chlorine. A condensed reaction pathway is shown in Fig. 2. The delay in particulate chlorine formation relative to that of bulk organics, as shown in Fig. 1, is consistent with the rate-limiting heterogeneous DHF production (Holt et al., 2005; Zhang et al., 2014). Under high NO_x conditions, the peroxy radical product from the chlorine-addition pathway could react with NO to form a cyclic hemiacetal chloronitrate or an alkoxy radical that would undergo ring-opening reactions. Compounds resembling chloronitrates (e.g. ~~$\text{ONO}_2\text{-C}_{12}\text{H}_{18}\text{ClO}_2\text{C}_{12}\text{H}_{18}\text{ClO}_3\cdot\text{I}$~~ for dodecane) were tentatively identified in the particle-phase using the FIGAERO but they were not well separated from the shoulder of nearby organonitrate peaks (e.g. ~~$\text{ONO}_2\text{-C}_{12}\text{H}_{21}\text{O}_4\text{C}_{12}\text{H}_{21}\text{O}_5\cdot\text{I}$~~), as shown in Fig. S9. Select C_{2-6} organochlorides were well-separated from nearby peaks and confirmed by the distinct Cl isotopic signal, the thermograms of which are shown in Fig. S10. The most abundant gas-phase ~~chlorinated~~-organic chlorine compounds observed were products of ring-opening reaction pathways such as $\text{C}_2\text{H}_3\text{ClO}_2$ and C_{4-6} compounds. Small amounts of $\text{C}_2\text{H}_2\text{Cl}_2\text{O}_2$ were also observed.

Organochloride formation is expected to be lower under humid conditions, where DHF formation is inhibited (Holt et al., 2005; Zhang et al., 2014; Ziemann, 2011). Evidence consistent with organochloride suppression under humid condition was observed for dodecane SOA only, where the organochloride (including chloronitrates) mass fraction decreased from 0.15 (Exp. 11, < 5 % RH) to 0.13 (Exp. 12, 67 % RH) as measured by the FIGAERO-CIMS. The mass fraction of the -Cl functional group decreased from 1.8 E^{-2} to 1.6 E^{-2} as measured by the FIGAERO-CIMS (Table S1) or from 1.4 E^{-2} to 1.1 E^{-2} as measured by the ACSM (Table 1) as the RH increased. No clear differences were observed for octane or decane SOA, which may be due to the less extreme RH conditions investigated, uncertainties with organochloride ion identification in the CIMS, or the lower organochloride concentrations observed in Exps.1-8, which is especially challenging for chloride quantification using the ACSM.

DHF ozonolysis can compete with chlorination. For instance, under typical marine boundary layer (MBL) conditions, the chlorine-initiated oxidation was estimated to be a significant sink of 2,5-DHF, accounting for 29 % of the reaction in the presence of OH and O_3 (Alwe et al., 2014). In contrast, only 1.8 % of 2,3-DHF consumption was attributed to Cl radical chemistry in the MBL, owing to the increased reactivity of 2,3-DHF (relative to 2,5-DHF) towards ozone and OH radicals (Alwe et al., 2014). The reported alkane-OH reaction mechanisms expect thes formation of substituted 2,3-DHF (Ziemann, 2011). The alkane-derived organochloride yield under ambient conditions is therefore expected to be smaller in the presence of elevated RH and O_3 levels. Although ozone can impose an upper limit on alkane SOA yields and oxidation state, suppressing the multigenerational OH-alkane oxidation chemistry (Zhang et al., 2014), the continued gas-phase processing of OH-alkane and DHF-ozonolysis products via H-abstraction by chlorine radicals could counteract these limitations.

The gas-phase alkane-Cl oxidation products formed under high NO_x conditions were dominated by organonitrates, which was also reflected in the dominance of organonitrates in the particles phase (see Table 1 and Section 3.2). Figure 3 shows the formation of early generation (e.g. hydroxynitrates, $\text{ONO}_2\text{-C}_n\text{H}_{2n+1}\text{O}$) and multi-generational (e.g. oxidized organonitrates, $\text{ONO}_2\text{-C}_n\text{H}_{2n-5}\text{O}_4$) oxidation products from different alkane precursors. Like the bulk particle phase composition, gas-phase compounds derived from smaller alkane precursor were more oxidized given similar oxidation conditions (e.g. NO, NO_2 , and Cl_2): the signal of oxidation products with similar oxygen numbers (and higher

oxidation state) peaked earlier into the photooxidation period for smaller precursors (e.g. $\text{ONO}_2\text{-C}_8\text{H}_{11}\text{O}_4$ vs. $\text{ONO}_2\text{-C}_{12}\text{H}_{19}\text{O}_4$ in Fig. 3). As oxidation continued, driven primarily by gas-phase chemistry (Aimanant and Ziemann, 2013), the importance of fragmentation reactions increased relative to that of functionalization reactions (Lambe et al., 2012). The heterogeneous oxidation of SOA (Bertram et al., 2001; George and Abbatt, 2010), which is expected to drive the oxidation of very large ($n>30$) alkanes (Lim and Ziemann, 2009b), may also contribute to oxidation and fragmentation observed here, but its impacts are beyond the scope of this work. Assuming a uniform CIMS sensitivity, Figure 4a shows that the gas-phase was dominated by C_3 to C_5 organic nitrates. Figure 4b shows that the OS_C increased while n_C decreased as photooxidation continued, indicative of fragmentation reactions. ~~The relative abundance of these small, oxidized organic nitrate compounds increased as the VOC precursor length decreased.~~ In addition to hydroxynitrates and hydroxycarbonyl nitrates, dinitrates and trinitrates were also observed. The CIMS was not sensitive towards simple, alkane-derived alkyl nitrates ($\text{ONO}_2\text{-C}_n\text{H}_{2n+1}$). The lack of sensitivity of the I reagent ion towards alkyl and keto nitrates has been reported previously for isoprene and monoterpene-derived organic nitrates (Lee et al., 2016).

15 3.2 Two-dimensional thermogram

The FIGAERO filter spectra are shown in Fig. 4 for octane (Exp 3), decane (Exp. 7), and dodecane (Exp. 11). A log-scale version of Fig. 4 is shown in Fig. S3. The spectra are calculated from the average desorption ion signals observed when the filter temperature was between 40 and 140 °C, As shown below and in Fig. 5, SOA components desorbed most effectively in this temperature range, with most organic ions having T_{max} within this temperature range. At desorption temperature above 140 °C, inorganic ions began to dominate the spectra. The C_{8-12} alkane-~~chlorine~~ SOA share many similarities towards the lower m/z (< 320) range which consisted of $\text{C}_{\leq 7}$ oxidized organic compounds. For larger alkane precursors, the particle phase composition was dominated by C_n organic nitrates, which are grouped by their degree of oxygenation (i.e. number of non-nitrate O atoms), “ O_x ”, as shown in Fig. 4c. O_1 to O_5 mono-nitrates, O_2 to O_4 dinitrates, and O_1 to O_3 trinitrates dominated each oxygenation group. O_6 to O_8 mono-nitrates were present in the particle-phase but were less abundant than the nearby O_2 to O_4 dinitrates (e.g. $(\text{ONO}_2)_2\text{-C}_{12}\text{H}_{20}\text{O}_2$ at m/z 447 $>$ $(\text{ONO}_2)_2\text{-C}_{12}\text{H}_{22}\text{O}_2$ at m/z 449 $>$ $(\text{ONO}_2)\text{-C}_{12}\text{H}_{17}\text{O}_6$ m/z 446 $>$

(ONO₂)-C₁₂H₁₉O₆ at *m/z* 448). An example of a C₁₂ mono-nitrate distribution is shown in Fig. S4. Assuming the same sensitivity towards the different organic nitrates observed, the organic nitrate abundance follows a bell-shaped distribution, similar to field observations for C₅ and C₁₀ organic nitrates derived from isoprene and monoterpenes, respectively (Lee et al., 2016). For dodecane mono-nitrates, the abundance peaked around O₃ and O₄ and decreased towards O₂ and O₅, as shown in Fig. S4. Dinitrate abundance decreased from O₂ to O₄. Trinitrate decreased from O₁ to O₃. Similar trends can be observed for octane and decane SOA. As the precursor length increased, the SOA appeared less oxidized, as shown in Fig. 4d, consistent with ACSM observations for *f*₄₄ (see Table 1 and Fig. S1), which is correlated with OS_C (Canagaratna et al., 2015). Simple hydroxynitrates (e.g. ONO₂-C_nH_{2n+1}O) were not observed in the particle phase as they were completely oxidized in the gas-phase, as shown in Fig. 3.

In addition to the identification of aerosol chemical composition, the FIGAERO-CIMS can be used to estimate the aerosol volatility using empirical correlations between C* and T_{max} (Lopez-Hilfiker et al., 2014, 2015). The particle-phase chemical composition and volatility distribution can be represented in several ways. For instance, desorption signals of select compounds can be normalized against the maximum and plotted on the same 1-D thermogram (ion signal versus filter temperature) to compare their relative volatilities (Lopez-Hilfiker et al., 2014). Scatter plots of oxygen number or O:C ratio versus carbon number colored by T_{max} or particle-phase mass fraction have been used to show changes in aerosol composition (Huang et al., 2018a; Lopez-Hilfiker et al., 2014, 2015). To show the differences of various types of thermal desorption products (i.e. monomers, thermal ~~fragmentation~~ decomposition products, and oligomers), averages of the 1-D thermograms can be shown (Huang et al., 2018a; Lopez-Hilfiker et al., 2015). Scatter plots of T_{max} or the ~~oxidation state of carbon~~ (OS_C) versus molecular weight have been used to distinguish monomers and oligomers for select compounds (Wang et al., 2016). Here we proposed a new framework to represent aerosol composition, relative volatility, and oligomer decomposition simultaneously using 2-D thermograms shown in Fig. 5a-e.

As illustrated in Fig. 5a for octane-chlorine SOA, the thermal desorption products ~~could~~ can be separated into 5 different groups. Region 1 (*m/z* < 350, 40 < T_{max} < 90 °C) was composed of a group of semi-volatile compounds with similar T_{max} values. This region also includes iodide-adducts which correspond to species that are too volatile to be present as molecular compounds in the particle phase and

are likely low-temperature decomposition products. ~~low molecular weight semi-volatile organic compounds, including C₁-to C₅-compounds that are not expected to be present in great amounts in the particle phase. These small organic compounds (detected as I⁻ adducts) were likely low temperature thermal fragmentation products.~~ Prominence of ions smaller than m/z 127 (i.e. ions generated not from iodide adduct formation but possibly acid exchange or charge transfer), including Cl⁻ and a range of organic ions, ~~was consistent with low-temperature thermal fragmentation~~ could be acid exchange or charge transfer products (as opposed to I⁻ adducts) of low-temperature decomposition products. Although I⁻ is a relatively soft ionization method (compared to electron impact ionization), collision-induced ion fragmentation and cluster dissociation cannot be ruled out as a potential source for non-adducts. Region 2 (350 < m/z < ~700, 40 °C < T_{max} < 120 °C) consisted of monomers, dimers, and some oligomers. Oligomerization may proceed via condensed-phase reactions between cyclic hemiacetal compounds, forming acetal dimers, or reactions between cyclic hemiacetal and 1,4-hydroxycaronyl compounds, forming hemiacetal dimers (Aimanant and Ziemann, 2013). Condensed-phase, acid-catalyzed isomerization of hemiacetal and acetal dimers is also possible (Aimanant and Ziemann, 2013). For OH-initiated oxidation of dodecane under high NO_x conditions, hemiacetals and nitrate hemiacetals are reported to dominate the oligomer composition (Schilling Fahnstock et al., 2015), where nitrate hemiacetals could form via the reactive uptake of hydroxy dihydrofuran and hydroxycarbonyl nitrate compounds (Schilling Fahnstock et al., 2015). The three oligomerization pathways are illustrated in Fig. S11. Ions consistent with acetal, hemiacetal, and nitrate hemiacetal compounds were observed in the particle phase using the FIGAERO-CIMS in regions 2 and 3. Oligomer formation via aldol condensation by highly oxidized compounds is also possible (Schilling Fahnstock et al., 2015). Oligomerization may also proceed through a NO₃-elimination, reverse esterification process involving two alkyl nitrate compounds to form a singly nitrate oligomer, which was recently proposed for α-pinene SOA, though the exact mechanism remains elusive. (Faxon et al., 2018).

— ~~that showed a~~ An overall positive correlation between T_{max} and molecular weight was observed in region 2., which has ~~A similar correlation was~~ also ~~been~~ reported for SOA derived from oleic acid (Wang et al., 2016) and from α-pinene (Faxon et al., 2018). In other words, overall, volatility decreased with molecular weight for compounds in region 2. However, within small m/z segments in region 2, the

correlation was not strictly linear and the T_{\max} varied cyclically. When the carbon and oxygen numbers were fixed (i.e. fixed O:C), the T_{\max} decreased (i.e. volatility increased) with increasing H:C (i.e. decreasing OS_c), as shown in Fig. 5e for C_{12} organic nitrates (e.g. $ONO_2-C_{12}H_{19-25}O_3-I$ from m/z 400 to 406) observed in dodecane-Cl SOA desorption. Although decreases in OS_c are often associated with increases in the aerosol volatility (Donahue et al., 2011; Kroll et al., 2011), fragmentation notwithstanding, the increase in H:C in each fixed O:C ion group was expected to decrease aerosol volatility. The increase in H:C was likely due to increased hydroxy functionalization over ketone functionalization, which should result in lowering of the saturation vapor pressure according to group contribution theory (Pankow and Asher, 2008). In addition, the T_{\max} decreased ~~going~~ from $O_3:C_{12}$ organonitrates (e.g. $ONO_2-C_{12}H_{21}O_3$, T_{\max} 95 °C) to $O_4:C_{12}$ organonitrates (e.g. $ONO_2-C_{12}H_{21}O_4$, T_{\max} 89 °C). The inconsistencies observed within small m/z segments may be due to loading-dependent T_{\max} shift (see Section 3.3), where T_{\max} ~~would~~ increases with mass loading. As shown in Fig. 4, the organonitrate ion intensities decreased from O_3 onwards. Overlapping of monomer and oligomer desorption peaks could also increase the apparent T_{\max} .

15 Region 3 ($T_{\max} > 90$ °C) consisted of thermal decomposition products across a wide m/z range. Select ions were present in both region 2 and region 3, resulting in bimodal thermal desorption, which can complicate T_{\max} estimation using the 2-D thermogram, especially when ions from the two desorption modes ~~show significant~~ overlap. The thermal decomposition products may be the result of reversible dissociation of oligomers (Faxon et al., 2018; Schobesberger et al., 2018) or the cleavage of C-O or C-C bonds, which has been observed in the thermal decomposition of monomeric organic acids (Stark et al., 2017). Additionally, SOA may exist in a “glassy” state (Koop et al., 2011), trapping volatile components (Perraud et al., 2012) that are released as the SOA mass is depleted. Region 4 (150 °C < T_{\max} < 170 °C) consists of mostly thermal decomposition products of the $(NH_4)_2SO_4$ seed particles. There was a clear gap between region 3 and 4. It is possible that the edge of regions 2 and 3 towards high T_{\max} range is the
25 FIGAERO-CIMS’s volatility detection limit for alkane-Cl SOA, where the energy required for vaporization exceeds that for thermal decomposition (Lopez-Hilfiker et al., 2014). Plateauing of T_{\max} towards the high m/z range of region 2 appeared to agree with this hypothesis, where further increases in molecular weight, carbon number, and the degree of oxidation translated to negligible T_{\max} increase.

Region 5 ($m/z > 700$) likely consisted of high molecular weight, low volatility oligomers. Region 5 therefore likely consisted of C_{24-36+} (dimers and above) compounds. Thermal desorption of some high molecular weight compounds at temperature much lower than expected ($T_{\max} \sim 80$ °C) was observed for decane SOA and dodecane SOA. No definitive molecular composition was determined for these ions due to low signal intensity and wide range of potential chemical ~~formulae/formulas. Based on proposed ammonium-catalyzed oligomerization reaction pathways for dodecane-OH SOA under high NO_x conditions, a hemiacetal dimer compound (m/z 457) could be produced (Schilling Fahnstock et al., 2015), which would be detected at m/z 584 using the I-FIGAERO~~

The region boundaries can vary depending on the SOA composition as well as mass loading, as will be discussed in Section 3.3. The distribution and general features of the regions are consistent for alkane-Cl SOA formed in different experiments (Fig. 5 and Fig. S8). Comparison of 2-D thermograms for octane-Cl SOA (Fig. 5a) and dodecane- Cl SOA (Fig. 5b) shows that the dodecane SOA contains unique, high molecular weight oligomers (~~$750 < m/z < 750$~~), which are accompanied by significantly stronger thermal decomposition features in region 3. Bimodal thermal desorption behavior was observed, as shown in Fig. 5d, which masked the volatility- m/z dependence expected for region 2. Compared to SOA formed under dry conditions (Fig 5b, Exp 11), SOA formed under humid conditions (Exp. 12, 67 % RH) contained less high molecular weight oligomers in region 5 and exhibited much less thermal decomposition behavior in region 3, as shown in Fig. 5e, where a more distinct T_{\max} - m/z correlation could be established as compared to Fig. 5d. RH-induced oligomer suppression has been reported for toluene and α -pinene SOA formation (Hinks et al., 2018; Huang et al., 2018a). The oligomer decrease under high RH could also be due to RH-volatility dependent organic vapor wall loss (Huang et al., 2018b). A clear m/z dependence of signal reduction under humid conditions as compared to the dry conditions is shown in Fig. S5. Additionally, SOA yield decreased (37 % for decane and 22 % for dodecane) under humid conditions while ozone production increased, which could be related to humidity-induced inhibition of 1,4-hydroxycarbonyl uptake and heterogeneous DHF formation (Holt et al., 2005). DHF is a key intermediate product for multigenerational oxidation chemistry and is reactive towards ozone (Zhang et al., 2014; Ziemann, 2011). Reduction in SOA yields under humid conditions has also been reported for dodecane-OH SOA formation (Schilling Fahnstock et al., 2015). The combined effects of DHF reduction

and ozone enhancement would suppress organic chloride formation, which was observed for ~~decane~~ (0-22% reduction relative to bulk organics) and dodecane (22%) SOA, as discussed in Section 3.1. shown in Table 1.

3.3 T_{\max} shift

5 As the desorption temperature increased above 140 °C, all dominant ions observed shared the same T_{\max} , except for some background ions (e.g. IHNO_3^-), as shown in Fig. 5a-c, which were identified to be related to the thermal decomposition of $(\text{NH}_4)_2\text{SO}_4$ seed particles. From this process, H_2SO_4 vapor molecules produced were either detected as $\text{H}_2\text{SO}_4\cdot\text{I}^-$ or were deprotonated to produce HSO_4^- , acting as a secondary chemical ionization reagent. Examples of 1st order (e.g. HSO_4^-), 2nd order (e.g. $\text{H}_2\text{SO}_4\cdot\text{HSO}_4^-$) and 3rd order sulfate (e.g. $(\text{H}_2\text{SO}_4)_2\cdot\text{HSO}_4^-$) clusters are shown in Fig. S6. It is worth noting that while the T_{\max} of sulfate ions was uniform within each filter desorption run, the T_{\max} varied between filter runs, which can be seen in Fig. 5a-c to be between 146 °C and 153 °C. ~~ACSM measurements of suspended sulfate concentrations and the integrated CIMS sulfate desorption signals suggest that the higher~~ Characterization experiments suggested that T_{\max} was associated with higher sulfate may increase with filter loadings, as shown in Fig 6a for pure levoglucosan aerosols and in Fig S7a for pure $(\text{NH}_4)_2\text{SO}_4$ aerosols. Fig. 6a shows the thermograms for $\text{H}_2\text{SO}_4\cdot\text{I}^-$ and $\text{H}_2\text{SO}_4\cdot\text{HSO}_4^-$ ions at different filter loadings for pure $(\text{NH}_4)_2\text{SO}_4$ aerosols, where T_{\max} increased from 136 °C to 149 °C as the filter loading increased by 258 %. Whereas the T_{\max} -mass loading correlation appeared to be linear for pure $(\text{NH}_4)_2\text{SO}_4$, as shown in Fig S7b for T_{\max} between 136-149 °C, a roughly sigmoidal correlation was observed for pure levoglucosan, as shown in

15 Fig 6b, where T_{\max} increased quickly from 43 to 62 °C as filter loading increased from 0.2 to 0.8 μg . Using the lowest filter loading tested as the basis for calculating a mass loading ratio (LR_{mass}), it can be shown that the sulfate T_{\max} varied linearly with loading in Fig. 6b.

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~~The~~ T_{\max} shift phenomena have been observed in several FIGAERO-CIMS studies (D'Ambro et al., 2017; Gaston et al., 2016; Huang et al., 2018a; Lopez-Hilfiker et al., 2015; Thompson et al., 2017). Explanations vary for the observed T_{\max} shifts. For example, pinonic acid ($\text{C}_{10}\text{H}_{16}\text{O}_3$) identified in Pinene-pinene ozonolysis SOA had a much higher T_{\max} (40 °C) than expected from calibration ($T_{\max} < 32$ °C), which was attributed to interactions between pinonic acid and other SOA components, causing a

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decrease in the measured apparent vapor pressure (Lopez-Hilfiker et al., 2015). However, no matrix effects were reported for the pinonic acid T_{\max} value (now around 65 °C instead of < 32 °C) obtained from a synthetic mixture of organic acid calibrants (Thompson et al., 2017), where some interactions between different organic molecules might have been expected. Whereas the pure compounds are shown to have sharp monomodal desorption peaks (Lopez-Hilfiker et al., 2014), the field campaign-average thermograms for individual compounds have broader desorption peaks (Thompson et al., 2017), which could be due to the presence of isomers (Thompson et al., 2017), variations in filter loading, differences in aerosol viscosity (Huang et al., 2018a), or interferences from oligomer decomposition products (Lopez-Hilfiker et al., 2014). Another T_{\max} shift example was reported for ambient biomass burning measurements, where the levoglucosan T_{\max} varied between 58 to 70 °C, in range of the 61.5 °C literature value (Lopez-Hilfiker et al., 2014) and the values observed here (41-65 °C), between 5 pm to 10 am over the course of the campaign (Gaston et al., 2016). Between 10 am to 7 pm, the levoglucosan T_{\max} was significantly higher at 100 °C, which was attributed to thermal decomposition of oligomers produced from acid-catalyzed heterogenous reactions, as indicated by the increase in sulfate ion intensities during the same period (Gaston et al., 2016). It was not clear if the sulfate ions measured were derived from sulfuric acid or from the decomposition of $(\text{NH}_4)_2\text{SO}_4$, which could change the assumption made for aerosol acidity. A T_{\max} shift was also observed for isoprene SOA, where the mass and T_{\max} of non-nitrated OA decreased with increasing NO_x concentration (D'Ambro et al., 2017). A recent investigation reported increases in T_{\max} for α -pinene ozonolysis SOA produced under dry conditions compared to SOA produced under humid conditions (Huang et al., 2018a). A positive correlation between aerosol loading and T_{\max} was reported for the first time, and the uniform thermal desorption peak shape assumption was questioned (Huang et al., 2018a). The loading dependence was reported to plateau at around 2 to 4 μg (converted from CIMS ion intensity assuming maximum sensitivity, i.e. that of formic acid), similar to observations for levoglucosan standards as shown in Fig 6b, possibly due to saturation effects. Because increased oligomer content was observed under dry conditions, the authors suggested that viscosity effects were responsible for the observed T_{\max} shift (Huang et al., 2018a). It should be noted that plateauing of the T_{\max} -loading dependence was demonstrated using averaged values, where ions were lumped based on carbon number. Those that had less than or equal to 10 carbons were designated as monomers, which

likely included desorption ions across multiple desorption regions (see Fig. 5). This categorization was perhaps too broad, and the loading dependence of individual ions could be lost after averaging. In contrast, the T_{\max} of oligomers, which were defined as compounds that contained more than 10 carbons—thus a more precisely defined group—only began to plateau at higher concentrations.

5 The T_{\max} mass dependence was also observed for alkane-Cl SOA. For Exp.6, three filters were collected and analyzed. The first filter was collected at 3 SLPM for 45 mins, followed by the second filter at 3 SLPM for 30 mins, and afterwards the third filter at 3 SLPM for 15 mins. The ratios of the unit-mass integrated ion signals during the desorption period for the first two filters relative to that of the third filter are shown in Fig. S8a. The associated 2-D thermograms are shown in Fig. S8b-d. Compounds in the
10 T_{\max} - m/z dependence region (Region 2) showed a 10 to 20 °C T_{\max} increase from the lowest filter loading to the highest filter loading conditions. T_{\max} of sulfate-related ions increased from 149 °C to 172 °C with filter loading. The increase of enhancement ratio with m/z , as shown in Fig. S8a, reflects the changes in the composition of suspended aerosol in the chamber over time. Between the first (high-loading) filter collection and the third (low-loading) filter collection, volatility-dependent vapor wall loss may lead to a
15 disproportionate decrease in high molecular weight, low volatility compounds (Huang et al., 2018b; Krechmer et al., 2016), resulting in increasingly greater enhancement towards the high m/z region shown in Fig. S8a. The correlation between T_{\max} shift and integrated desorption signal for organics was not linear, unlike for ammonium sulfate, which may be due to matrix or saturation effects as previously suggested (Huang et al., 2018a). T_{\max} -loading dependence may differ for individual FIGAEROs due to
20 design variations or artifacts, such as sample distribution within the filter matrix or non-uniform heating, which would result in different aerosol evaporation kinetics (Schobesberger et al., 2018). Overall, our results show that the T_{\max} for organic and inorganic compounds varies with loading, which needs to be accounted for when estimating aerosol component volatility from the empirical correlations between T_{\max} and C^* using the FIGAERO-CIMS.

25 4 Conclusion

Environmental chamber experiments were carried out to investigate the chlorine-initiated oxidation of C_8 -
12 linear alkanes under high NO_x conditions. Rapid SOA formation and ozone production were observed.

SOA yields increase with precursor length, consistent with alkane-OH SOA formation. Under similar oxidation conditions, alkane-Cl SOA exhibited more hydrocarbon-like characteristics as the alkane precursor length increased, as indicated by the ACSM measurements. This bulk SOA observation is consistent with gas- and particle-phase CIMS measurements, which identified more oxidized reaction products derived from smaller alkane precursors. CIMS measurements also ~~confirmed-suggested~~ that organonitrates dominated the gas- and particle-phase composition. ~~Using the ACSM and the FIGAERO-CIMS,~~ Trace amounts of alkane-derived organochlorides were observed using the ACSM and the FIGAERO-CIMS, likely produced via chlorine-addition to the heterogeneously produced dihydrofuran compounds. Organochloride and bulk SOA production were suppressed under humid conditions, whereas ozone production increased. Under such conditions, the SOA yields observed for chlorine-initiated oxidation of octane (0.24), decane (0.50), and for dodecane (1.10) were still much higher than those observed for OH-initiated oxidation of the respective alkanes. Overall, these results show that chlorine-alkane oxidation could be an important pathway for SOA production and ageing, especially in highly polluted environments replete with alkane, NO_x, and reactive chlorine emission sources.

15 A clear mass loading dependence for T_{\max} from FIGAERO-CIMS data was demonstrated using levoglucosan, ammonium sulfate, ~~aerosols~~ and alkane-Cl SOA, indicating that the quantitative assessment of C^* from T_{\max} using the FIGAERO-CIMS needs to account for variations in filter loading. A unit-mass-resolution 2-D FIGAERO-CIMS thermogram framework was developed. The 2D thermograms demonstrate a clear relationship between molecular weight and volatility of aerosol components, and RH-induced suppression of oligomer formation. When used in conjunction with high-resolution ion fitting, the 2D thermogram can be a powerful tool for interpreting the chemical composition and volatility distribution of particle-phase compounds.

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Table and Figures

Table 1. Summary of Experimental Conditions and Results

Exp #	VOC	NO ^a	NO ₂ ^a	Cl ₂ ^a	RH	SOA	Y _{SOA} ^b	f ₄₄ ^c	f ₅₇ ^d	f _{NO₃} ^e	f _{HCl+} ^{ef}	O ₃ ^{fg}
1	Octane	35	2	40	5 >	19.5	0.28	1.1 E ⁻¹	<u>1.4</u> E ⁻²	1.3 E ⁺	1.1 to 1.3 E ⁻²	56
2	Octane	1	36	40	5 >	11.0	0.16	1.0 E ⁻¹	<u>1.6</u> E ⁻²	1.1 E ⁺	0.7 to 1.1 E ⁻²	69
3	Octane	17	19	40	5 >	16.6	0.24	1.5 E ⁻¹	<u>1.1</u> E ⁻²	1.2 E ⁺	0.8 to 1.0 E ⁻²	56
4	Octane	17	19	40	35	16.8	0.24	1.0 E ⁻¹	<u>1.3</u> E ⁻²	1.3 E ⁺	1.1 to 1.4 E ⁻²	60
5	Decane	32	0	40	5 >	68.3	0.84	1.0 E ⁻¹	<u>1.6</u> E ⁻²	1.3 E ⁺	0.7 to 1.1 E ⁻²	53
6	Decane	0	34	40	5 >	43.1	0.45	7.3 E ⁻²	<u>1.7</u> E ⁻²	1.3 E ⁺	0.9 to 1.0 E ⁻²	61
7	Decane	19	18	40	5 >	64.7	0.80	1.3 E ⁻¹	<u>1.6</u> E ⁻²	1.2 E ⁺	0.9 to 1.2 E ⁻²	51
8	Decane	19	17	40	40	40.7	0.50	8.2 E ⁻²	<u>1.7</u> E ⁻²	1.2 E ⁺	0.7 to 1.2 E ⁻²	57
9	Dodecane	35	1	40	5 >	148.6	1.65	2.1 E ⁻¹	<u>1.5</u> E ⁻²	0.8 E ⁺	0.6 to 0.8 E ⁻²	42
10	Dodecane	0	34	40	5 >	112.8	1.25	6.3 E ⁻²	<u>2.5</u> E ⁻²	1.0 E ⁺	0.8 to 1.4 E ⁻²	54
11	Dodecane	17	18	40	5 >	126.4	1.40	6.8 E ⁻²	<u>2.4</u> E ⁻²	1.1 E ⁺	0.9 to 1.4 E ⁻²	46
12	Dodecane	20	17	40	67	98.8	1.10	7.2 E ⁻²	<u>2.5</u> E ⁻²	0.9 E ⁺	0.7 to 1.1 E ⁻²	62

NO, NO₂, O₃, and Cl₂ concentrations are in ppb. RH is in %. SOA concentration is in μg m⁻³. Y_{SOA}, f₄₄, f₅₇, f_{NO₃}, and f_{Cl} are dimensionless

- 5 (a) Initial concentrations
 (b) Y_{SOA} is calculated using the maximum SOA concentration and the initial precursor concentrations, which were 70 (octane), 81 (Decane), and 90 (Dodecane) μg m⁻³, assuming complete VOC consumption
 (c) Mass ratio of organic ion fragments at *m/z* 44 (presumably mostly CO₂⁺) to the sum of all organic ion fragments observed at peak SOA concentration. Used as a proxy for the SOA extent of oxidation
- 10 ~~(d)~~ Mass ratio of organic ion fragments at *m/z* ~~57~~5 (presumably C₄H₉⁺) to the sum of all organic ion fragments observed at peak SOA concentration. Used as a proxy for hydrocarbon-like organic aerosol
~~(e)~~(d) ~~Mass ratio of the NO₃ ion fragments (i.e. from ONO₂ functional group) to the organics ion fragments (bulk organics concentration)~~
- 15 ~~(f)~~(e) Ratio of particulate chlorine mass (estimated using HCl⁺ ion fragments in the ACSM) to ~~bulk organics concentration~~ mass. Lower value is the ratio observed at ~~bulk organics~~ organic mass peak and the higher value is the ratio observed at the particulate chlorine peak. Particulate chlorine and ~~bulk organics~~ peak at different times due to the rate-limiting heterogeneous production of dihydrofurans. Chloride concentrations were near detection limits for octane experiments and may be more sensitive towards vaporizer interference effects (Wang and Hildebrandt Ruiz, 2017; Hu et al., 2017)
- 20 ~~(g)~~(f) The amount of ozone observed when peak SOA concentration was observed

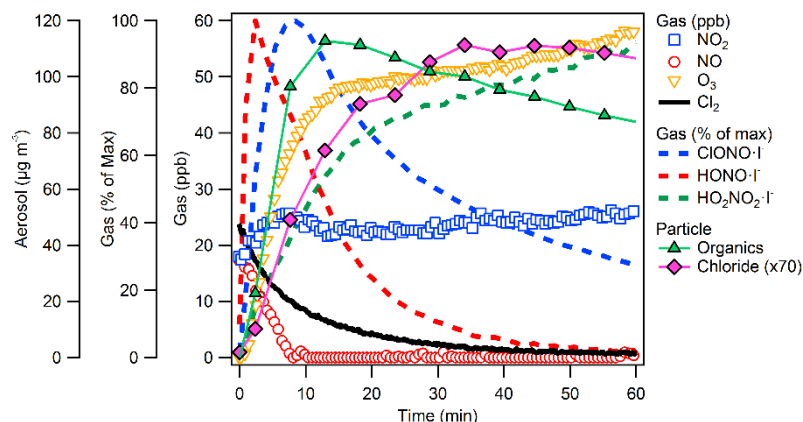


Figure 1: Representative trends of SOA and trace gas species during the photooxidation period. Data from dodecane oxidation (Exp. 11) are shown. Particulate chlorine concentrations were multiplied by 70 for ease of comparison. Ions consistent with HONO and HO₂NO₂ were observed, indicative of secondary HO_x chemistry. Formation of ClONO and ClNO₂ due to oxidation of NO₂ by Cl[•] was also observed.

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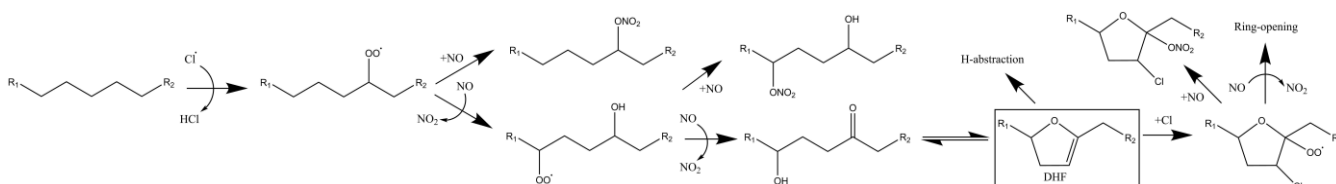
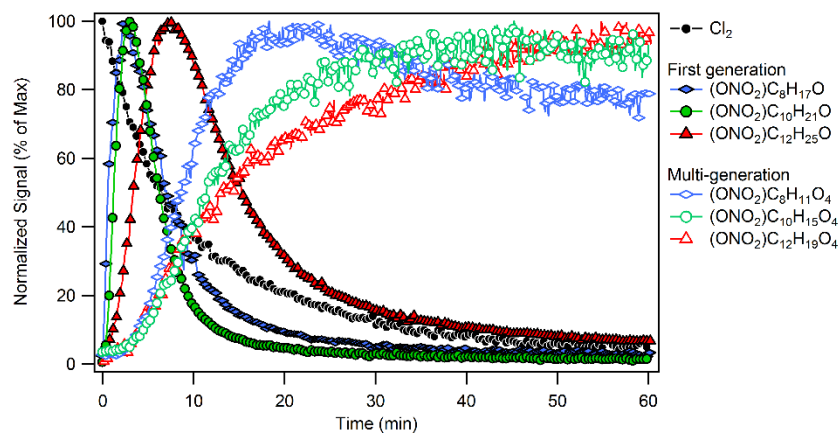
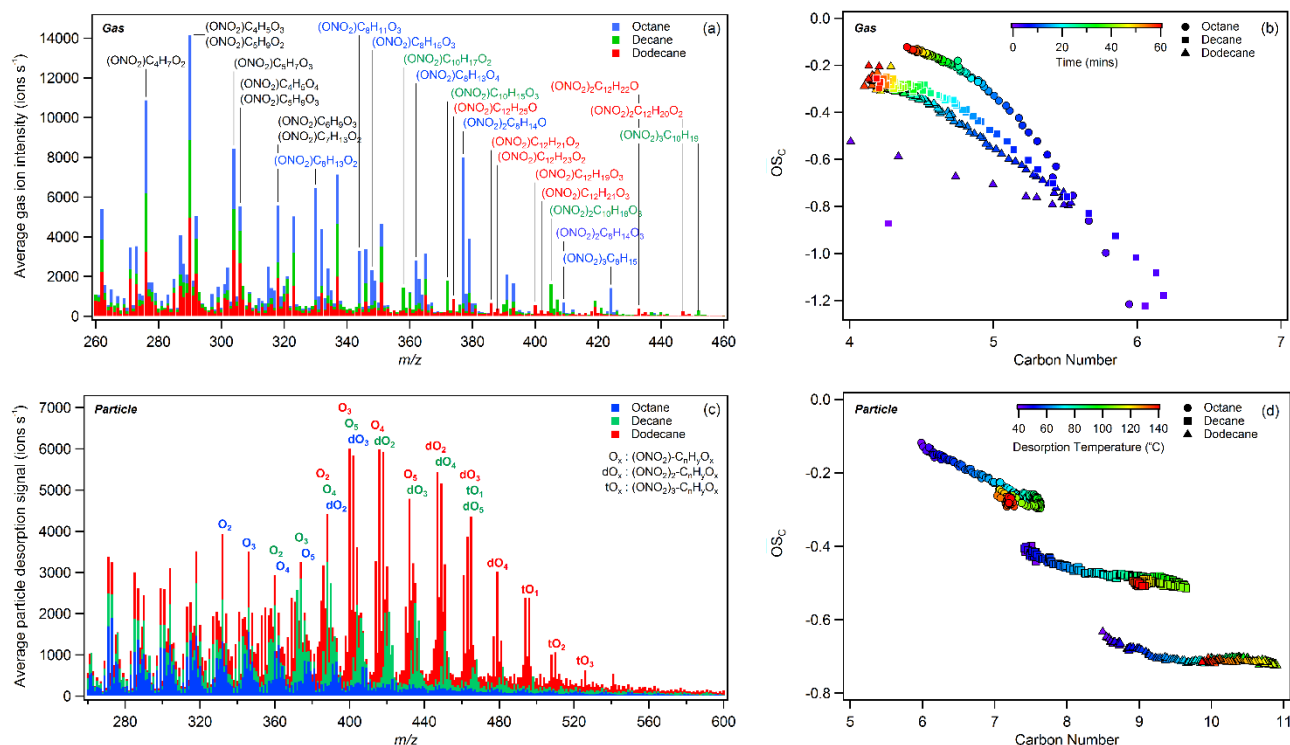


Figure 2: Formation pathway for chlorinated organics via chlorine addition to the DHF. H-abstraction from DHF is also possible. Ozone may also react with the double-bond on the DHF, competing with chlorine radicals.



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Figure 3: Trends of early-generation gas-phase oxidation products (hydroxynitrates) and multigeneration-oxidation products (hydroxycarbonyl nitrates) observed during chlorine-initiated oxidation of octane (Exp. 3), decane (Exp. 7), and dodecane (Exp. 11). Species shown were first normalized against the I⁻ reagent ion signal and then normalized against their respective maxima.



5 **Figure 4:** Comparison of the (a) average gas-phase composition during the oxidation period and (b) the increases in average OS_c of gas phase reaction products over the photooxidation period (0-60 mins), as well as the (c) average particle-phase composition and (d) the evolution of average SOA OS_c during FIGAERO desorption for octane (Exp. 3), decane (Exp. 7), and dodecane (Exp. 11). Color-coded ions in (a) and (c) indicate products that were much more abundant in reaction products derived from a particulate alkane precursor. In (b,c), O_x, dO_x, and tO_x were used as shorthand notations for oxidized organic nitrate, dinitrate, and trinitrates with x number of oxygens (excluding those from ONO₂). Sticks in (a) and (c) were not stacked, and no x-axis offset was applied during plotting. In (b), OS_c increased and n_c decreased as photooxidation continued, consistent with photooxidative fragmentation. In (d), SOA derived from larger alkane precursors appeared less oxidized, consistent with results shown in Table 1 and Fig S1. Methods used to calculate the average OS_c and n_c are detailed in the S.I.

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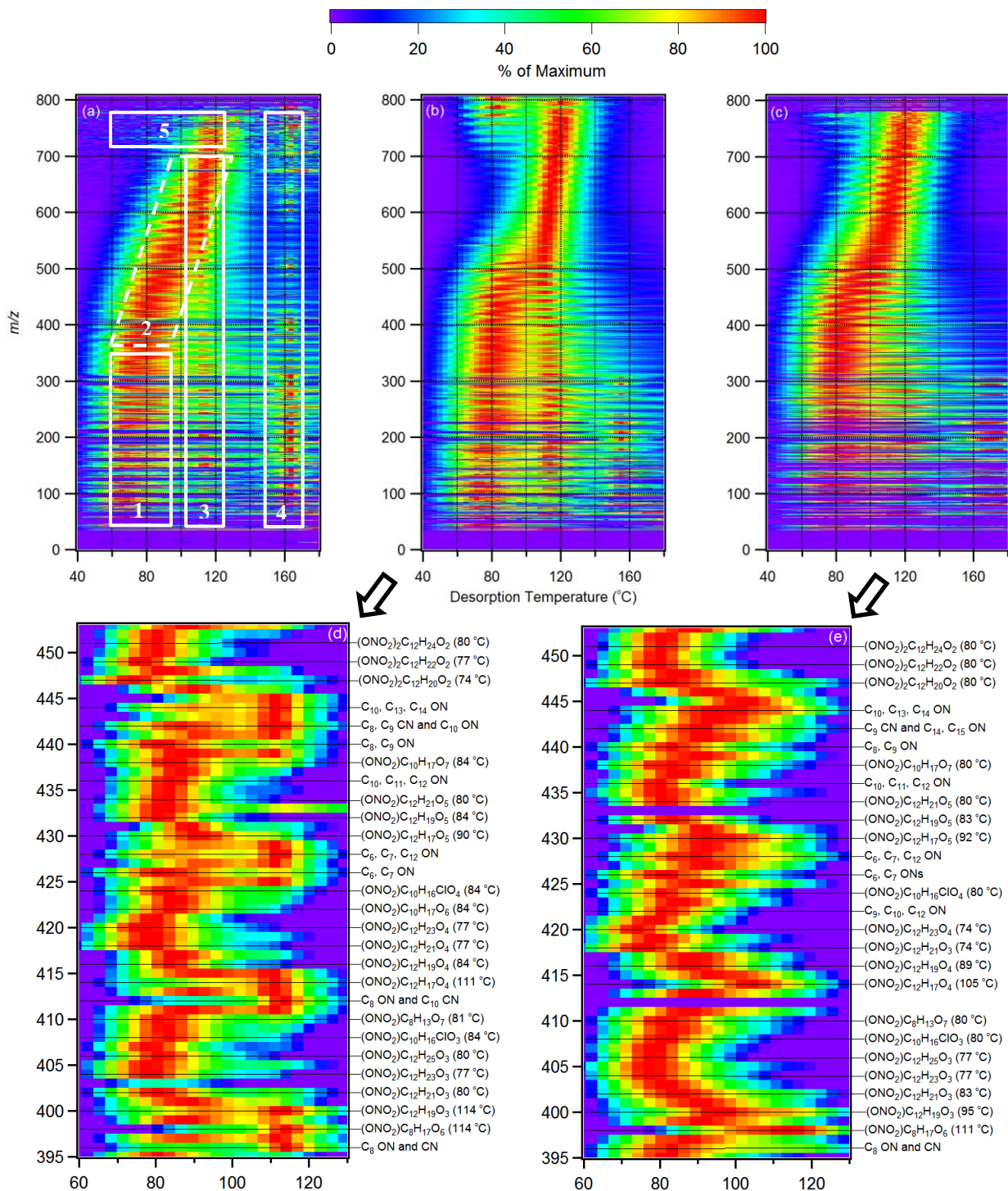


Figure 5: Comparison of two-dimensional thermograms for (a) octane-Cl SOA under low RH from Exp. 3, (b) dodecane-Cl SOA under low RH from Exp. 11, and (c) dodecane-Cl SOA under high RH (67 %) from Exp. 12. The color represents the ion intensity at a m/z as a percentage of the maximum desorption signal observed at that m/z . Different thermal desorption regions in (a) are dominated by (1) low-

temperature thermal fragmentation-decomposition products and non-adducts (2) monomers (3) oligomers and their decomposition products and (4) thermal decomposition of ammonium sulfate or extremely low volatility compounds. Region (5) is unresolved but appears to be thermally unstable oligomers. Region (2) and (3) can overlap, as shown in (d) for (b) and as shown in (e) for (c). At each nominal m/z , only the dominant ion is labeled in (d) and (e). If multiple ions of similar intensity were present, only general descriptions are given in the annotations, where “ON” stands for organonitrate and “CN” stands for chloronitrate. Non-nitrated organic ions were observed but not labeled because they were positioned in-between more intense organonitrates at neighboring m/z coordinates. T_{\max} values are included in parenthesis. Increasing the RH suppressed oligomer formation, enhancing the monomer features in (c) and (e) when compared with (b) and (d). The m/z values shown includes the chemical ionization reagent I (m/z 127).

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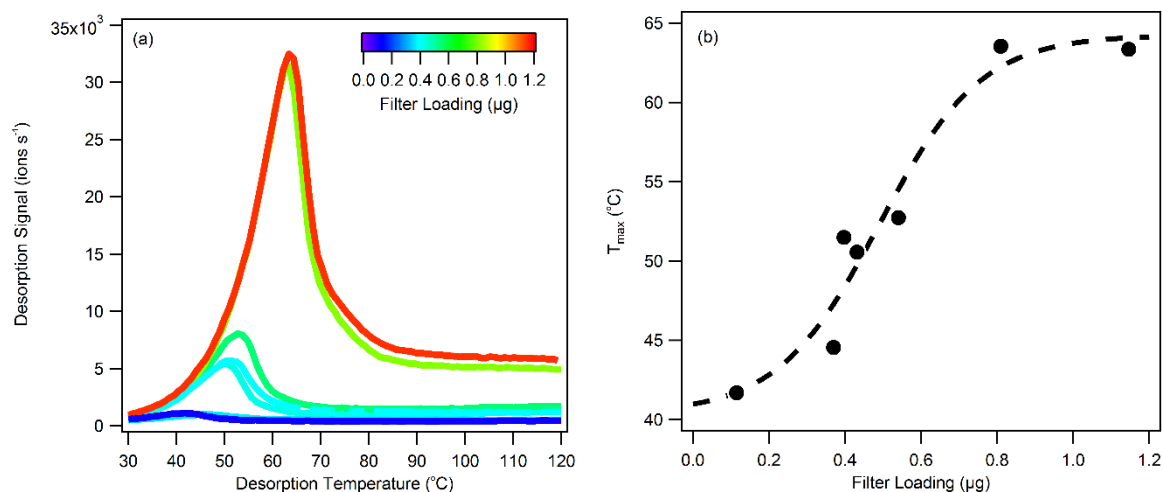


Figure 6: (a) The 1-D thermograms for two $(\text{NH}_4)_2\text{SO}_4$ -decomposition product ions levoglucosan ($\text{C}_6\text{H}_{10}\text{O}_5$) at different loading conditions and (b) the correlation between filter loading and T_{\max} . Levoglucosan aerosol was generated by nebulizing a $1.2 \text{ E}^{-2} \text{ M}$ aqueous solution. The aerosol was injected into the clean Teflon chamber, collected onto the FIGAERO filter, and analyzed. The T_{\max} -loading correlation for pure levoglucosan could be described by a sigmoid function, leveling off at 41 and 65 °C under very low and very high loading conditions, respectively. $\text{H}_2\text{SO}_4 \cdot \text{I}$ was the primary adduct and $\text{H}_2\text{SO}_4 \cdot \text{HSO}_4^-$ was a secondary ionization product. The lowest time-integrated desorption ion intensity for $\text{H}_2\text{SO}_4 \cdot \text{I}$ was used as the basis for calculating the loading ratio (LR_{mass}). The loading ratio for $\text{H}_2\text{SO}_4 \cdot \text{HSO}_4^-$ (not shown) is the square of that for $\text{H}_2\text{SO}_4 \cdot \text{I}$. (b) Linear regression fitting of T_{\max} as a function of the LR_{mass}

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